

U. S. DEPARTMENT OF AGRICULTURE.

Report No. 71.

SOME MUTUAL RELATIONS BETWEEN ALKALI  
SOILS AND VEGETATION.

BY

THOMAS H. KEARNEY, ASSISTANT PHYSIOLOGIST,  
*Division of Vegetable Physiology and Pathology,*

AND

FRANK K. CAMERON, SOIL CHEMIST,  
*Division of Soils.*



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## LETTER OF TRANSMITTAL

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U. S. DEPARTMENT OF AGRICULTURE,  
DIVISION OF VEGETABLE PHYSIOLOGY AND PATHOLOGY,  
*Washington, D. C., June 24, 1901.*

SIR: I have the honor to transmit herewith several papers on Some Mutual Relations between Alkali Soils and Vegetation, prepared by Mr. Thomas H. Kearney, of this Division, who was detailed to the work at the request of the Chief of the Division of Soils, and Dr. Frank K. Cameron, of that Division, and respectfully recommend their publication as Report No. 71 of the Department. The studies so far made in connection with the work discussed in these papers have brought to light some important facts and have opened lines of inquiry which promise to develop methods of dealing with alkali soils that will reduce their injurious effects on crops grown where such soils exist.

Respectfully,

ALBERT F. WOODS,  
*Chief of Division.*

Hon. JAMES WILSON,  
*Secretary of Agriculture.*

## LETTER OF SUBMITTAL.

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U. S. DEPARTMENT OF AGRICULTURE,  
DIVISION OF SOILS,

*Washington, D. C., June 24, 1901.*

SIR: I respectfully submit herewith the manuscript of a report prepared by Mr. Thomas H. Kearney and Dr. Frank K. Cameron to throw light upon problems encountered by the field parties of the Division of Soils in the soil survey of certain areas in the West affected with alkali. As this is treated largely from the physiological side, it seems proper that it should be transmitted by you for publication.

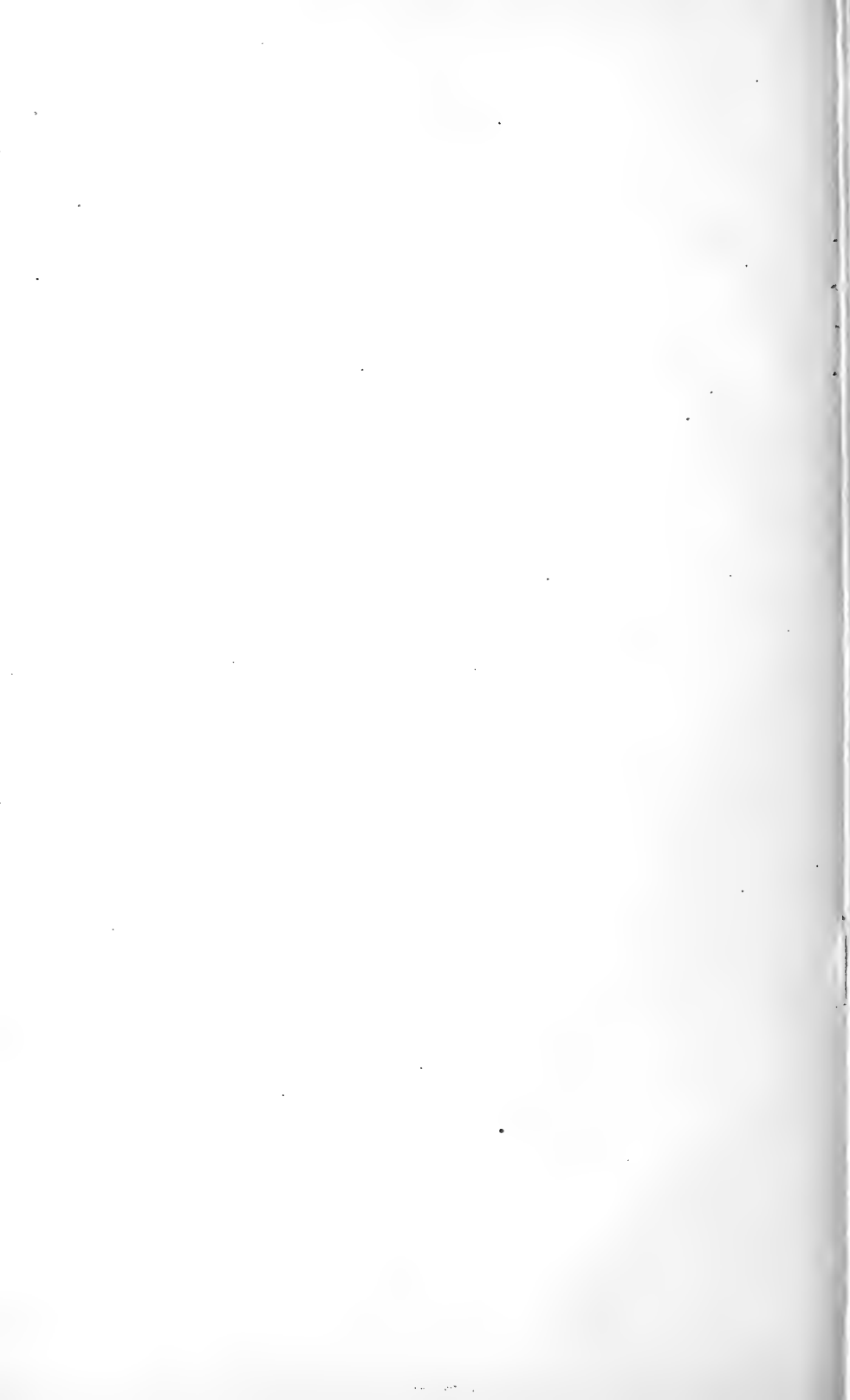
Respectfully,

MILTON WHITNEY,  
*Chief of Division.*

MR. ALBERT F. WOODS,  
*Chief, Division of Vegetable Physiology and Pathology.*

# CONTENTS.

	Page.
<b>The Effect upon Seedling Plants of Certain Components of Alkali Soils. By</b>	
<b>THOMAS H. KEARNEY and FRANK K. CAMERON:</b>	
Introduction .....	7
Methods of experiment .....	9
Salts employed .....	9
Plants selected for experiment .....	10
Details of manipulation .....	13
Determination of the limit of endurance .....	15
Results with pure solutions .....	19
Concentration maximum permitting survival of the roots .....	19
Concentration minimum prohibiting elongation of roots .....	24
Results with less soluble salts .....	25
Results with mixed solutions .....	27
Magnesium sulphate in mixtures .....	29
Magnesium chloride in mixtures .....	32
Sodium carbonate in mixtures .....	33
Sodium sulphate in mixtures .....	35
Sodium chloride in mixtures .....	36
Calcium chloride in mixtures .....	37
Sodium bicarbonate in mixtures .....	37
Calcium sulphate and calcium carbonate in mixtures .....	37
General significance of results with mixed solutions .....	40
Stimulating effect of dilute solutions .....	47
Economic importance of the results .....	52
Summary .....	54
Conclusion .....	55
Bibliography .....	56
<b>Formation of Sodium Carbonate, or Black Alkali, by Plants. By FRANK K.</b>	
<b>CAMERON:</b>	
Introduction .....	60
Creosote bush .....	61
Greasewood .....	63
Absorption of mineral constituents by the plant .....	65
Comparison of analyses .....	68
Summary .....	69
<b>Resistance to Black Alkali by Certain Plants. By FRANK K. CAMERON:</b>	
Introduction .....	70
Method of examination .....	70
<i>Distichlis spicata</i> .....	71
Isolation and identification of acid exudation .....	72
Hydroscopic salt on the plant surface .....	73
Selective absorption of soil constituents .....	73
Function of the acid exudation .....	74
Phosphorus in the plant .....	74
Ash analyses .....	75
<i>Suaeda intermedia</i> and <i>Atriplex bracteosa</i> .....	76
Summary .....	77



# SOME MUTUAL RELATIONS BETWEEN ALKALI SOILS AND VEGETATION.

## THE EFFECT UPON SEEDLING PLANTS OF CERTAIN COMPONENTS OF ALKALI SOILS.

By THOMAS H. KEARNEY and FRANK K. CAMERON.

### INTRODUCTION.

Everyone who is familiar with alkali soils knows that their character varies greatly in different localities, one salt or combination of salts predominating over others which may be present.<sup>1</sup> Sometimes sodium carbonate, the dreaded "black alkali," is relatively abundant as compared with the other soluble soil components. In other cases this salt may be entirely absent or present merely as a trace, while one or more of the "white alkali" salts, e. g., sodium chloride or sodium sulphate, plays the most important part.

It is also known that these salts are not all equally injurious to vegetation. Sodium carbonate, for instance, is generally believed to be much more harmful than any other salt of common occurrence, owing probably to its pronounced corrosive action on the plant tissues. Gypsum, or the dihydrate of calcium sulphate, on the other hand, is harmless and even beneficial in ordinary cases. Experiments with solutions of chemically equivalent strength show very marked differences in the action of different salts upon plant growth. Hence the question whether the salt forming the greater part of the soluble components of a given soil is, to take a concrete case, the very injurious sodium carbonate or the relatively harmless sodium chloride, may often determine whether that soil is utterly useless or quite valuable to the farmer.

It becomes, therefore, a question of great importance to everyone who is concerned with soils which contain an appreciable amount of alkali to know definitely the relative harmfulness of the salts both severally and in mixtures, since the latter is the condition under which they almost invariably occur in nature.

Field observations will give some idea of how the soluble salt components compare in this regard. But the conclusions are necessarily somewhat vague and unsatisfactory; for in the field and under the conditions that are found in nature it is practically impossible to study

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<sup>1</sup>See Bulletin No. 17, Division of Soils, U. S. Department of Agriculture (1901).

the effect of any one soil component. It is rare indeed that the "alkali" is composed of but one salt or chemical individual. And, as will be brought out later, it is entirely impossible to predicate anything definite as to the action of a mixture of salts upon a plant from a previous knowledge of the effects produced by each single salt. Conversely, it is equally impossible to draw conclusions as to the action of any one of a mixture of salts from observations of the effects produced by the mixture itself.

The more exact methods of the laboratory are necessary in order to give us precise knowledge, and with this end in view the present investigation was undertaken. It is not claimed that the results so far obtained are in all respects conclusive. The fact that only two species of plants were employed in these first experiments is sufficient indication that they are not. In physiological research nothing is more dangerous than generalization from the behavior of one or a few species of plants to that of plant life as a whole. It is a well-established fact that species differ widely in their reaction to a given chemical or physical condition. Witness the fact that seaweeds will thrive in water containing 1.5 to 3 per cent of sodium chloride, and that salt marshes, whose soil is saturated with water containing nearly or quite as much of this salt, often support a luxuriant vegetation, while the average crop is killed by a much more dilute solution of sodium chloride. Certain plants show a marked aversion to limestone soils, while other species are almost entirely limited to soils having a high content of lime.<sup>1</sup> But it is needless to multiply illustrations of so familiar a phenomenon.

That a similar diversity is manifested by different cultivated crops in their sensitiveness to various mineral salts when present in the soil solutions is well known. Therefore we can not safely predict, until experiments with many different plants have been made, that the order of harmfulness of the alkali salts here established for two plants will be found to hold for all or even many of those which are commonly cultivated in the alkali regions. But, as it is obviously essential to the satisfactory prosecution of alkali soil work that a definite standard for comparison of the salts be established, there need be no further apology for the presentation of these first results of what it is hoped will become an exhaustive investigation.

In the progress of the work numerous data were accumulated which appeared to possess a more than ordinary degree of scientific interest, especially as relating to the chemical theory of the dissociation of electrolytes in solution and to the recently published hypothesis that various salts, or rather their dissociated ions, enter into compounds

<sup>1</sup> The interesting subject of "lime-loving" and "lime-avoiding" plants has been much discussed by European botanists. It is synoptically treated by Drude (*Handbuch der Pflanzengeographie*, p. 51) and by Schimper (*Pflanzengeographie*, p. 105). The latter author gives an extensive bibliography.

with the proteids of the protoplasm of plants and animals, which "ion proteids" play a highly important part in life processes and phenomena. This aspect of the subject will be treated particularly in discussing the significance of the experiments with mixed solutions.

## METHODS OF EXPERIMENT.

### SALTS EMPLOYED.

In the selection of a series of salts for investigation the experience of members of the Division of Soils in field and laboratory served as a guide. Salts were used which have been determined as forming definitely injurious components of alkali soils and as occurring in sufficient quantity to be of practical importance. In about the order of their general abundance in the Western United States these are sodium chloride ( $\text{NaCl}$ ), sodium sulphate ( $\text{Na}_2\text{SO}_4$ ), sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), sodium bicarbonate ( $\text{NaHCO}_3$ ), magnesium chloride ( $\text{MgCl}_2$ ), magnesium sulphate ( $\text{MgSO}_4$ ), and calcium chloride ( $\text{CaCl}_2$ ). Incidentally, experiments were made with gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), calcium carbonate ( $\text{CaCO}_3$ ), calcium bicarbonate [ $\text{Ca}(\text{HCO}_3)_2$ ], and with magnesium carbonate ( $\text{MgCO}_3$ ), and bicarbonate [ $\text{Mg}(\text{HCO}_3)_2$ ], as well as with an aqueous solution of carbon dioxide ( $\text{CO}_2$ ), the last in order to test a theory that suggested itself during the experiments with carbonates and bicarbonates.

In preparing and standardizing the solutions much assistance was rendered by Mr. Seidell, of the Division of Soils.

The solutions were invariably made with salts manufactured by Baker & Adamson, and found to be practically chemically pure, dissolved in distilled water.<sup>1</sup> They were made up in each case on the basis of a normal solution—i. e., of a gram-equivalent per 1,000 c. c. of

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<sup>1</sup> The water used in all experiments was distilled through a tin worm and was collected and stored in Winchester quart bottles of practically insoluble glass. A conductivity test showed this to be an unusually pure water, but in order to establish this point beyond doubt, a portion of this same water was redistilled from glass, the first and last portions being of course discarded. A test of the distillate showed it to possess about twice as great conductivity as that which had been distilled only once from the tin. A comparison of cultures of lupines in the water which had been only once distilled with that which was redistilled showed practically no difference in the amount of growth made by the roots. As Galeotti has lately shown [*Biol. Centralbl.*, 21, 329 (1901)], the oligodynamic action of relatively concentrated "colloidal" solutions of metals disappears in the presence of weak solutions of electrolytes. Thus a solution of copper containing 1 gram-atom of metal per 126,000 liters of water produced no effect upon *Spirogyra* in the presence of a 0.01 per cent solution of sodium chloride, and a solution of 1 gram-atom of copper per 63,000 liters of water acted only after twenty-four hours, although in the absence of the electrolyte the toxic effect of the colloidal copper solution is manifested at a dilution of 1 gram-atom of copper per 126,000,000 liters of water. (See footnote, p. 50.) Hence it is practically certain that in the experiments described in this report no complications were to be feared from the possible presence of a trace of metals in the water used.

solution. In other words, in the case of monovalent compounds, one gram-molecule was contained in a liter of solution, while in the case of bivalent compounds, a half gram-molecule was present.<sup>1</sup> In this way only is a really instructive and fair comparison of the effects of different salts obtainable. Many experiments made in times past in which comparisons were based upon simple percentages of solute to solvent by weight are for this reason of far less value than if normal solutions had been employed. In order to study comparatively those effects produced by different electrolytes which are not dependent upon their respective chemical natures, but which are common to them all and due only to their active masses (such, for instance, as effects due to the osmotic pressure existing in the solution), it is obviously necessary to take into consideration the number of reacting weights of the electrolyte introduced and the amount of electrolytic dissociation which takes place. That is to say, one must consider the concentration of the solution with respect to the number of reacting chemical equivalents, molecules, or ions which may be present. Moreover, attempts to study comparatively the effects produced by different kinds of ions in the solution can only be made by approaching the subject in this manner. But in all statements in this report of the concentration of a given solution both fractions of a normal solution and parts of salt to 100,000 of solution are given in order that the results may be readily intelligible to readers who are familiar with one or the other method, as the case may be.

The method pursued in these experiments was to make and carefully standardize a large volume of a normal solution of each salt and then dilute to the required strength as occasion demanded.

In beginning the experiments the limit for each salt as determined by investigators in the field was first tried, but immediately showed itself to be too high. So lower and lower concentrations had to be tested until the critical one was reached.

#### PLANTS SELECTED FOR EXPERIMENT.

For a variety of reasons the white lupine (*Lupinus albus*) was employed in nearly all the experiments, although subsequently alfalfa (*Medicago sativa*) was introduced for comparison. The lupine has a seed of good size, averaging 10 to 12 mm. in greatest diameter. As an abundant supply of nutritive material is stored in the thick seed leaves, there is no danger of starvation of the seedlings in experiments of short duration such as those here described. The lupine seeds germinate readily, sending out a vigorous radicle with clean,

<sup>1</sup>Dandeno [Bot. Gazette 32, 229 (1901)] has recently called attention to a certain amount of confusion which has existed among both chemists and physiologists as to the preparation of a normal solution, and it has seemed wise to describe in detail the procedure followed in this investigation.



bright, white surface. If the seeds are germinated in a proper medium (sphagnum or peat moss saturated with water was actually employed) the root is usually straight or nearly so. These characteristics are important, as they permit the easy and accurate measurement which is essential to a determination of the amount of growth made during a given period. The white lupine has the further advantage of being a favorite subject for experiment with plant physiologists, so that numerous data for comparison are available.

In one series of experiments lupine plants were used which had been grown for eleven days in a prepared culture solution, and had not only developed a considerable root system, but had unfolded two or three leaves in addition to the seed leaves. In these plants all the processes essential to the life of a mature individual were undoubtedly in full activity. As a rule, however, a much earlier stage of growth was preferred, as clearly affording a more sensitive index of the effect of solutions. Experiments with older plants indicated that they are less delicate registers of toxic effect. An additional advantage in using very young plants is that they are practically independent of the substratum so far as food supply (that is, the mineral ash constituents) is concerned, that stored in the thick cotyledons answering all purposes. Consequently the confusion which would unavoidably arise if a culture solution of several salts containing the necessary elements of plant food were introduced is avoided by the employment of seedlings.

Lupine seedlings were transferred directly from the sphagnum, in which they had germinated twenty-four to forty-eight hours previously, to the solution in which the experiment was to be made. In this stage of growth the seed leaves are still closely appressed one to another, and are pale yellow in color. The initial root is 3 to 6 cm. long, and shows as yet no indication of the appearance of lateral branches. Care was taken to keep the moss so wet as to preclude a normal development of root hairs; and in this respect the result would be the same if the radicles had been immersed in water immediately after germination. It was desired to render as slight as possible the change of conditions in transferring from one medium to the other. There is every reason to believe that under these circumstances the amount of injury sustained by the plants as a result of the change of substratum was reduced to a minimum.<sup>1</sup>

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<sup>1</sup> Wolf demonstrated [Landwirthsch. Versuch-st., 6, 203. (1864)] that plants which had been grown in soil until a considerable root system was developed and then shifted to an aqueous solution (as in the experiments of De Saussure and others) could not be depended upon to give as satisfactory results as plants which had been cultivated from the moment of germination in aqueous solutions. But in the case of seedlings transferred from loose wet sphagnum to water before any lateral roots had appeared no difficulty of this sort need be apprehended.

From the experiments of others with plants cultivated in salt solutions it would appear that *Lupinus albus* agrees pretty closely in point of sensitiveness with other large-seeded Leguminosæ, e. g., peas (*Pisum sativum*), beans (*Phaseolus vulgaris*), and, at least in some cases, with the horse bean (*Vicia faba*).<sup>1</sup>

In order to determine how closely plants of the same family correspond in their resistance to toxic effect, and at the same time to obtain data as to the behavior of a plant whose economic importance in arid regions is inestimable, a number of experiments were made with alfalfa (*Medicago sativa*). Here we have to deal with a plant whose seeds are many times smaller than those of the white lupine (1.5 to 3 mm. in greatest diameter). The radicle of the alfalfa seedling is correspondingly small and delicate, and hence requires more careful manipulation than does that of *Lupinus*. Alfalfa seeds were germinated in wet blotting paper, and were transferred to the solutions when the radicles were 1 to 2 cm. long.

A basis for comparison of the effects of toxic solutions upon plants of very different character and relationship is afforded by Heald's investigations of the action of extremely dilute solutions of hydrochloric acid upon seedling peas, pumpkins, and maize.<sup>2</sup> This author calculates that while one part of hydrogen ions (liberated by dissociation) in 6,400,000 parts of water killed the root tips of the pea (*Pisum sativum*),<sup>3</sup> one part in 3,200,000 was required to produce a similar effect upon the pumpkin (*Cucurbita pepo*) and one part in only 1,600,000 to destroy the root tips of maize (*Zea mays*). In other words, maize offers four times and the pumpkin twice as much resistance to the toxic effect of hydrochloric acid as do peas and lupines.

These results emphasize the importance of extending the present investigations to other plants of as widely different botanical relationship as possible. It is also of great moment that experiments be made with different stages of growth of the same plant, from the germinating seed to some point near maturity. It is as certain that the same kind of plant at various periods of development differs in its reaction to a given salt solution as that the reaction of the same plant to the same solution will be affected by variations of temperature and, perhaps, of illumination.<sup>4</sup>

<sup>1</sup> But not always, for True [Annals of Botany, 9, 372, (1895)] found the white lupine "more strongly affected by a 0.25 per cent solution than is *Vicia faba* by one of 1 per cent KNO<sub>3</sub> content." He finds *Pisum* likewise more sensitive than *Vicia faba*.

<sup>2</sup> Bot. Gazette, 22, 136 (1898).

<sup>3</sup> The white lupine appears to be about equally sensitive to H-ions, for Kahlenberg and True [Bot. Gazette, 22, 91 (1896)] determined its limit of endurance in a solution of HCl to be  $\frac{1}{3400}$  normal, while later Kahlenberg and Austin [Journ. Physical Chem., 4, 557 (1900)] fixed upon  $\frac{1}{5300}$  normal as a more accurate limit.

<sup>4</sup> Storp [Landwirthsch-Versuchsst., 13, 76 (1884)] found zinc sulphate to be extremely injurious to germinating seedlings when exposed to the light, but harmless, or nearly so, in the dark.

The practical value of such a development of these studies is indicated by certain conditions to which agriculture in alkali regions is subject. It is well known that while at the beginning of the season the salt components are often pretty equally distributed through a considerable depth of soil and are in consequence comparatively harmless, the increased evaporation which accompanies increased temperatures and decreased atmospheric moisture as the season advances draws these salts to the surface of the soil, where they often effloresce and form "crusts" (especially in the case of sodium carbonate and sodium sulphate). Hence older plants are frequently exposed to the action of much more concentrated solutions than the same individuals when younger had to contend with. Furthermore, the accidents of irrigation may materially alter the alkali content of a soil in the midst of the growing season of a crop. It is therefore to be hoped that this important extension of the investigation may soon receive attention.

#### DETAILS OF MANIPULATION.

The manner of preparing the solutions and the plants to be cultivated has already been described. A few words about methods and details followed in the experiments are in order.

To contain the solutions, glass vials nearly 3 cm. in diameter and holding about 70 c. c. of liquid were used. In the experiments with lupines, only one plant was suspended in each vial by means of a hole bored through a close-fitting thin cork stopper, the aperture being entirely closed by means of cotton batting. Protection against undue evaporation from the upper portion of the plant was secured by placing several vials in a glass jar containing a little water and inverting another jar over the whole. The plant was so adjusted in the cork that 1 to 3 cm. of the terminal portion of the radicle was immersed in the solution, the uppermost portion of the radicle extending through the vapor-saturated space between solution and stopper, while the hypocotylary section was invested with moist cotton.

In the case of alfalfa five or six plants were inserted in each vial in the following manner: A piece of aluminum wire was passed through the cork stopper in such a way as to allow it to be raised or lowered at discretion. On the portion of the wire included in the vial five or six small loops were made of proper size to hold in place each a seedling plant, with its seed leaves resting on the loop and its root immersed in the solution.

The duration of the culture in the salt solution was generally limited to twenty-four hours, as it was usually possible at the end of that period to determine accurately whether the root tip had been killed or not. Frequently, however, the plants were returned to the solution for a second period of equal duration in order to remove all doubt upon this point.<sup>1</sup> If at the end of that period no growth had taken

<sup>1</sup>In this particular, as in others, the experimental methods outlined by Kahlenberg and True [*Bot. Gazette*, 22, 87, 90 (1896)] have been followed, as it was desirable to make as close comparison as possible with their results.

place since the first examination, it was regarded as reasonably certain that the root tips had perished, and a less concentrated solution was tried. To obviate the possibility of mistaking a temporary condition of plasmolysis for final loss of vitality the roots were in earlier experiments transferred, after twenty-four hours, from the salt solution to distilled water; but this precaution soon proved to be needless. In all the experiments a control culture in distilled water was maintained under conditions of temperature and illumination identical with those of the salt cultures. As a matter of course, the growth of the roots is by no means as rapid in distilled water as in ordinary river water or in a prepared culture solution.

It was sought to keep the external conditions as nearly as possible uniform during the entire series of experiments and a temperature of 19° to 21° C. was maintained in the laboratory.<sup>1</sup>

The rate of growth during the period of experiment was ascertained by marking the radicle with india ink just before placing it in the solution. The mark, which was made as fine as was compatible with permanency, was placed at a distance of 15 mm. from the root tip in the case of the lupines and 10 mm. in the case of alfalfa (*Medicago*) so as safely to include the entire zone of active growth in the primary root.<sup>2</sup> This method of measuring the growth of roots was employed by Sachs in his classical studies upon the growth of primary and lateral roots,<sup>3</sup> and has been widely adopted by plant physiologists.<sup>4</sup> By comparison of the marked root with a ruled surface the amount of growth during any given period can be determined with all the accuracy necessary in experiments of the kind here described.<sup>5</sup>

By using a considerable number of individual plants in each experiment with each solution (usually five in case of *Lupinus* and ten or twelve in case of *Medicago*) it is believed that the variant due to individual differences in vigor has been practically eliminated.<sup>6</sup>

<sup>1</sup> In this connection Klemm [Jahrb. f. wiss. Botanik, 28, 659 (1895)] calls attention to the great variability exhibited by plants as to their limit of endurance in solutions of acids of definite concentration if other external conditions be varied. Askenasy [Ber. deutsch. bot. Gesellsch., 8, 61 (1890)] describes the effect upon the growth of roots produced by different temperatures or by a variation of temperature during a limited period of time.

<sup>2</sup> Sachs determined the length of the growing portion, in the case of roots of other Leguminosae, to be 8 to 10 mm. for *Vicia faba* and 3.5 to 6.5 mm. in *Pisum sativum*. [Arb. d. bot. Inst. Würzburg, 1, 413 to 419 (1873): Gesammelte Abhandl., 2, 803 (1893)]

<sup>3</sup> Gesammelte Abhandl., 2, 778.

<sup>4</sup> For example, Kahlenberg and True use this method in all their experiments with plants in solutions of toxic substances. [See Bot. Gazette, 22, 88 (1896)]

<sup>5</sup> Askenasy [Ber. d. deutsch. bot. Gesellsch., 8, 64, (1890)] shows that this method of marking causes a retardation of growth during the first hour thereafter, but that this is overcome after two hours. Consequently the method could be used without hesitation in these experiments, although it is sometimes attended by disadvantages when the phenomena of growth itself are studied.

<sup>6</sup> More than 2,500 seedlings of *Lupinus albus* and 700 of *Medicago sativa* were employed in the whole series of experiments.

Indeed, that this was the case was pretty effectually shown by several repetitions of the experiments with most of the solutions. It is also indicated by the general regularity with which toxic effect is shown to increase with every increase in concentration of the solution of each salt. By several times repeating experiments with solutions of approximately the critical strength the above-mentioned source of error due to fluctuations in temperature, etc., was likewise reduced to a minimum.

#### DETERMINATION OF THE LIMIT OF ENDURANCE.

In ascertaining the degree of concentration of a given salt solution which will just permit the root tips to retain their vitality during the period of experiment, one must of course be able to determine also the point at which death definitely occurs. The death point is evidently to be sought far below the degree of concentration which permits no elongation whatever to occur during the period of experiment, for often radicles, of which the marked zone had increased in length several millimeters (even 6) at some time during the experiment, were indubitably dead at the end of twenty-four hours.<sup>1</sup> The mere fact of elongation, irrespective of the time in which it has taken place, does not therefore determine the concentration of a salt solution in which roots will survive, although sometimes useful in ascertaining whether the root is absolutely dead at the end of a given period. It is to the general condition of the apical portion of the root that we must look for a criterion. While it is sometimes difficult to describe those symptoms which denote the death of the root tip, it is comparatively easy to recognize them after one has acquired sufficient experience with the behavior of plants grown in toxic solutions.

One of the most easily detected of the phenomena accompanying death in plants is final loss of turgor due to excessive plasmolysis. In other words, the tissues lose their water, and are unable to make good the loss, even when restored to normal conditions. This is due primarily to a change in the osmotic equilibrium of the plant cells. Ordinarily, through the controlling activity of the protoplasm, a sufficient osmotic pressure is maintained in the sap cavity of the cell to

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<sup>1</sup>Experiments were made with solutions of a strength known to be fatal, yet permitting some elongation during twenty-four hours. Sodium sulphate (0.05 normal), sodium carbonate (0.02 normal), and magnesium chloride (0.05 normal) were selected, and in every case it was found that elongation ceased entirely after three to five hours. In a water control, on the other hand, growth was still progressing at the end of six hours, and an examination at the end of twenty-four hours showed that it had been pretty equally distributed throughout the entire period. These results as to toxic action correspond with Sachs's statement [*Landwirthsch. Versuchsst.*, 1, 219 (1859)]; *Gesammelte Abhandl.*, 1, 430 (1892)] that "roots appear to lose more and more the power of absorbing water containing salt the longer they are in contact with it."

retain the necessary minimum of water. But through various influences, such as exposure of the tissues to a salt solution whose concentration exceeds a certain limit, this power of adjustment may be temporarily lost. In such cases a considerable proportion of the cell water diosmoses through the ectoplasm, and the protoplast in consequence shrinks away from the cell walls, to which it is normally closely applied. If the unfavorable condition persists, this temporary plasmolysis may become permanent, and the cell is killed outright.

Such disorganization due to extreme plasmolysis can usually be detected immediately by an examination of the plant tissues with the microscope, and is one of the best indications of death.<sup>1</sup> Roughly, however, injury of this nature is sufficiently indicated after a certain lapse of time by loss of rigidity and elasticity in the plant or part of a plant affected; in other words, it becomes flaccid. If, for example, a root thus rendered flaccid by culture in a salt solution fails to regain its turgor after being transferred to water or to a nutritive solution, it may safely be considered as injured beyond recovery. This was found to be the most satisfactory test of death employed.<sup>2</sup>

The color of the tissues is often a useful symptom of destructive changes. Thus all the sodium salts employed, when given in suffi-

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<sup>1</sup> "The only externally perceptible change [indicating death] is in many cases collapse, a more or less strong, irregular recession of the protoplast from the cell wall, which does not, however, accompany by any means all reactions of substances which occasion death." [Klemm, *Desorganisations-erscheinungen der Zelle*. Jahrb. für wiss. Botanik, 28, p. 657 (1895).]

<sup>2</sup> Sachs [Arb. bot. Inst. Würzburg, 1, 386: *Gesammelte Abhandl.*, 2, 774] mentions as an indication of the approaching death of the root tip the disorganization of the cells of the root cap, which becomes mucilaginous. This was noted in many cases, but was not found to be a practical test of complete loss of vitality. Another indication of injury to the apical portion of the root is a sharp bend near the tip, which is very different from the normal gentle curvatures. This usually appears where loss of turgor from plasmolysis is not manifested. While indicating injury, this symptom by no means necessarily implies complete loss of vitality and, therefore, does not serve our purpose as a symptom of death. Solutions of a certain concentration of magnesium sulphate, magnesium chloride, and calcium bicarbonate were found to produce this phenomenon in a marked degree. In the case of the salt last mentioned the roots continued to grow slowly in distilled water, during a second period of twenty-four hours. True [Ann. of Botany, 9, 377, (1895)] alludes to these "sharp curves characteristic of injury."

Another means of detecting loss of vitality in protoplasm, to which, however, recourse was not had in the progress of this work, is its coloration when dead by means of nigrosin, which does not color and does not injure living protoplasm. See Pfeffer [Ueber Aufnahme von Anilinfarben in lebende Zellen. Unters. aus d. bot. Inst. Tübingen, 2, 268, 269], who found in experiments with roots of duckweed (*Lemna*) and with *Spirogyra* that nigrosin is not absorbed by cells while alive. Living root hairs exposed for three days to a 0.5 per cent solution of this stain assumed no coloration whatever, while hairs after death when similarly treated readily absorbed it.

cient amount, decolorized the tissues of the apical portion of the root. This lost its normal brilliant white appearance<sup>1</sup> and assumed a lurid-whitish color. In the case of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and of sodium bicarbonate ( $\text{NaHCO}_3$ ) there occurred a marked clearing of the tissues similar to that produced by the hydrates of potassium and sodium, the root tips becoming nearly transparent. This change is completed long before any loss of turgor is apparent. Magnesium salts (chloride and sulphate) discolored the surface of the roots, producing brownish spots which gradually spread over the whole surface.<sup>2</sup> The difference in character of physiological effect produced by salts of the same acid in the case of sodium on the one hand, and of magnesium on the other, is very great when gauged by these external appearances.

Another effect produced by some of these salts is an irregular enlargement of a portion of the root. This is very marked in the case of calcium chloride, in a solution of 0.3 normal or thereabouts. The root just above the tip develops a fusiform swelling of which the greatest transverse diameter (2 to 3 mm.) lies 5 to 10 mm. from the apex of the root. A less marked formation of this sort is sometimes produced by magnesium chloride, and even by other salts.<sup>3</sup>

It is well to emphasize once more the fact that the death of the tip of the primary root, and not that of the plant as a whole or even of the entire root, was taken in these experiments as the indicator of the toxic action of solutions. The condition of the distal 10 to 20 mm.

<sup>1</sup> The "shining white opaque appearance which is characteristic of all healthy roots and which is due to air contained in the intercellular spaces." (Sachs, Landwirthsch. Versuchsst., 1, 216; Gesammelte Abhandl., 1, 427).

<sup>2</sup> Mettenius [quoted by Wolf in Landw. Versuchsst., 7, 202, (1865)] found that these spots, which appear on the roots of both the bean and maize when placed in solutions of magnesium salts, are due to a coagulation of the contents of the epidermal cells, which he did not, however, further describe. Wolf remarks that they do not appear upon plant roots in magnesium salt solutions if a salt of potassium, ammonium, or calcium be present.

<sup>3</sup> Sachs (Arb. bot. Inst. Würzburg, 1, 411, 412; Gesammelte Abhandl., 2, 800) describes swellings of apparently similar character which developed upon roots grown in moist air and watered at long intervals. Wolf [Landw. Versuchsst., 6, 218 (1864)] found that a concentrated solution of potassium sulphate acted in the same manner. "The root tips soon swell in the solution; the form of the root finally resembles that of the root of a tuber-bearing plant. Such swellings arise in particular abundance where lateral roots will break through." The action of a one-fourth per cent solution of potassium nitrate upon roots of *Lupinus albus* as described by True [Ann. of Botany, 9, 374 (1895)] is exactly similar to that of calcium chloride. "Swellings appeared near the tips and the ends tapered suddenly to sharp points. On the other hand, the growth in thickness was much greater than normal, the radicles above the swellings reaching the size of large radicles of *Vicia faba* of the same length."

only was necessarily involved.<sup>1</sup> In the more dilute solutions which are still considered toxic, because destroying the root tip, the proximal portion of the root and the upper part of the plant are often not conspicuously injured by twenty-four or forty-eight hours' exposure. After a certain lapse of time lateral roots are sometimes put forth and grow vigorously in a solution (especially of calcium chloride) which had killed the apical portion of the primary root.

This power of gradual accommodation on the part of the plant to a solution which at first checked its growth and even destroyed the sensitive tissues of the root tip has often been remarked. It is but a step from this to the well-known fact that by gradually increasing the strength of a salt solution in which plants are cultivated they can be made to endure a degree of concentration which would soon be fatal if administered directly.<sup>2</sup> It follows that the limits of endurance here recorded for *Lupinus albus* are merely those of its root tip, selected as being the most sensitive indicator, and are in some cases lower than the limits which would denote death of the plant as a whole. Furthermore, the limit of endurance for the entire plant could undoubtedly be still further elevated by gradually increasing the strength of solution in which the plants are cultivated.

But our present investigation aims merely at a comparison of the relative toxicity of the various "alkali" salts, to attain which the simplest and readiest means are to be preferred. A standard for further comparisons, rather than a thorough investigation of the problem in all its ramifications, is the end of the present paper.

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<sup>1</sup> This was likewise the objective of the experiments of Kahlenberg and True [Bot. Gazette, 22, 88, (1896)]. In order to obtain results closely comparable with theirs, especially as bearing upon the hypothesis of electrolytic dissociation, their mode of procedure has been closely followed in this as in other details. In advocacy of this method of determining toxic action, Professor True writes: "Repeated experiments for years have convinced me that the method used gives the most delicate and easily managed test that I know of for bulky objects like *Lupinus* roots."

Coupin [Rev. Gén. de Botanique, 10, 177 (1898)] criticises the work of Kahlenberg and True, previously quoted, to the effect that it is impossible to accurately determine the toxic limit of a solution in the short period of experiment (twenty-four hours) allowed by those authors. However, as Professor True observes, it was not the point at which the whole plant succumbs, but that which marks the death of the zone of growth in the primary root, which formed the objective of his experiments. Coupin's method was to grow his plants for several days in the solutions to be tested, taking the strongest solution in which the plant as a whole continued to grow after the first few hours as marking the limit of endurance ("équivalent toxique"). It is obvious, therefore, that no direct comparison is possible between the results obtained by Coupin on the one hand and by Kahlenberg and True, as well as those here recorded, on the other. Coupin's limits of endurance being necessarily much higher.

<sup>2</sup> Thus Stange [Bot. Zeitung, 50, 292 (1892)] found that root tips of *Lupinus albus* and *Phaseolus vulgaris* soon died if exposed directly to a 0.5 per cent solution of potassium nitrate, but by gradually increasing the concentration they could be made to endure nearly 1 per cent without death of the protoplasm.



## RESULTS WITH PURE SOLUTIONS.

## CONCENTRATION MAXIMUM PERMITTING SURVIVAL OF THE ROOTS.

By applying the methods and tests outlined above it was possible to determine with a reasonable degree of accuracy the limit of concentration for each of the salts in pure solution in which the root tips of young seedlings of white lupine could just survive. It is believed that, like conditions being maintained and the same plant in the same stage of development being used, the limits will not be materially altered by further experiment. Moreover, it is regarded as not improbable that the salts will be found toxic in about the order stated below if other plants or other stages of growth of the same plant be tested with them. The limit of endurance in a solution of each particular salt will doubtless be higher or lower for different objects, but the general sequence of harmfulness should remain practically unaltered, so far as the higher plants are concerned. Experience alone can demonstrate the correctness of this assumption.

The limit of concentration permitting roots of white lupine to retain their vitality during twenty-four hours is, for each of the more important readily soluble "alkali" salts, as follows, the limit being stated both in parts of salt per 100,000 of solution and in fractions of a normal solution:

TABLE I.—*Results of experiments with pure solutions.*

Name of salt.	Degree of concentration.	
	Parts per 100,000 of solution.	Fractions of a normal solution.
Magnesium sulphate.....	7	0.00125
Magnesium chloride (1).....	12	.0025
Sodium carbonate.....	26	.005
Sodium sulphate (2).....	53	.0075
Sodium chloride (3).....	116	.02
Sodium bicarbonate (4).....	167	.02
Calcium chloride.....	1,377	.25

NOTES.—(1) With magnesium chloride the limit of endurance (for the whole plant), as determined by Coupin [Rév. Gén. de Bot., 10, 188 (1898)], is 0.8 per cent, while with magnesium sulphate the limit is 1 per cent, thus reversing the order of toxicity for the two salts as given above. Wolfo (Landw. Versuchsst., 6, p. 214) notes the strongly toxic effect of magnesium solutions upon roots of bean and maize. The brown coloration of the surface of the radicle, induced by these salts, appeared a few hours after immersion. Wolf's suggestion that the very poisonous effect of magnesium sulphate may be due to the decomposition of the salt by excretions of the roots can not be regarded as possessing great probability. His experiments, which were designed primarily to ascertain the volume of water absorbed by the plant from solutions of various salts of different concentration, are considered by him to indicate that the cell wall [ectoplasm] is less permeable to sulphates than to other salts (l. c., p. 217). Loew (Bul. No. 18, Div. Veg. Phys. and Path., p. 42) found that Spirogyra died after four or five days of immersion in a 0.1 per cent solution of magnesium sulphate, but remained alive for a long period in equivalent solutions of sulphates of potassium, sodium, and calcium. Similarly a 1 per cent solution of magnesium nitrate killed a smaller Spirogyra in six to twelve hours, while the nitrates of potassium, sodium, and calcium, in solutions of corresponding strength, did not destroy the plant. The peculiarly poisonous action of salts of magnesium described by Loew is explained by him on the hypothesis that calcium forms intimate compounds with proteids, and that these are essential to the organization and life of the cell-nuclei and chloroplasts of the higher plants. Consequently, if magnesium is supplied without calcium to plants, especially in the form of readily soluble salts, such as chloride, nitrate, and sulphate, the acids of the magnesium salts would be attracted by the calcium which formed part of the nuclear proteid compounds. The latter would consequently be disorganized, magnesium being unable to take the place of calcium in proteid compounds without fatal disturbances of equilibrium in the cell. As evidence for this hypothesis is added the corrective effect of the addition of lime to either soils or culture solutions in which plants are suffering from magnesium poisoning, and the further fact that plants suffer less in culture solutions from which both calcium and magnesium are absent than in such as contain magnesium but no calcium. It must be observed, however, that the chemical rationale of this theory

rests upon the assumption that calcium is a stronger base than magnesium, and will exert a greater attractive force upon acids, while it ignores the application of the mass law to the distribution of an acid between two bases, which itself accounts very satisfactorily for the facts observed.

(2) Of sodium sulphate Wolf (Landw. Versuchsst., 6, pp. 210, 213) indicates that solutions of more than 0.05 per cent are toxic to roots of the bean (*Phaseolus vulgaris*). Loeb [Am. Journ. Physiology, 3, 393 (1900)], found sodium sulphate to be more poisonous than sodium chloride to eggs of a fish (*Fundulus heteroclitus*). This he attributes to a precipitation of calcium from its ion proteid compounds in the protoplasm, a reaction effected through the sulphions dissociated by sodium sulphate.

(3) The minimum toxic concentration for sodium chloride, the same plant and the same methods being used, is placed about three times as high (one-sixteenth normal) by True [Amer. Journ. Sci., ser. 4, 9, 187 (1901)]. As the experiments with sodium chloride here described were repeated several times, without variation in the result, no explanation for this discrepancy is apparent.

Many experiments have been made with sodium chloride as to its effects upon plants. It may be of interest to refer to some of those in which limits of endurance have been determined, especially as these are in all cases much higher than that given above for root tips of *Lupinus albus*. Storp [Biedermann's Centralbl., 13, 76 (1884)] found that sodium chloride in a solution of greater concentration than 0.01 per cent retarded the germination of seeds. Eschenhagen [Ueber den Einfluss von Lösungen verschiedener Concentrationen auf den Wachsthum der Schimmelpilze (1889)], quoted by Stange in Bot. Zeitung (1892, p. 255), gives the following limits for the active growth of fungi in solutions of sodium chloride and of sodium nitrate:

Fungus.	Per cent sodium chloride.	Per cent sodium nitrate.
<i>Aspergillus</i> .....	17	21
<i>Penicillium</i> .....	18	21
<i>Botrytis</i> .....	12	16

Richter [Ueber die Anpassung der Süßwasseralgen an Kochsalzlösungen Flora, 75, 4 (1892)] found that *Zygnema stellinum genuinum* lived two months in a 6 per cent solution of sodium chloride added to a culture solution, and more than a year when the sodium chloride solution was 2 per cent or weaker. De Freitag [Archiv für Hygiene, 11, 68 (1890)] is authority for the statement that *Bacillus tuberculosus* lived three months, and the typhus *Bacillus* six months in a saturated solution of sodium chloride. Coupin [Révue Gén. de Botanique, 10, 177 (1898)] obtained the following limits for various plants in solutions of sodium chloride:

Plant.	Per cent limit of endurance.	Per cent in different solution.
Wheat .....	1.8	0.5
Peas .....	1.2	.25
White lupine .....	1.2	-----
Maize .....	1.4	-----
Vetch .....	1.1	-----

According to W. Sigmund [Landw. Versuchsst., 47, 1 (1896)] the maximum concentration of NaCl solutions endurable by germinating seeds of cereals is 0.5 per cent, of legumes 0.3 per cent, of rape 0.1 per cent. Loew [Bul. 18, Div. Veg. Phys. and Path., p. 19] found that *Spirogyra* suffers in a solution containing 0.5 per cent of sodium chloride.

(4) Carbonic acid ( $\text{HCO}_3$ ) is here regarded as a monovalent acid, so that a gram molecule (instead of one-half of a gram molecule) to the liter has been used in making up normal solutions of sodium bicarbonate. To prevent inversion to the normal carbonate ( $\text{Na}_2\text{CO}_3$ ) [see Cameron and Briggs, Bul. 18, Div. of Soils, 1900; also Jour. Physical Chem., 5, 537 (1901)] solutions of the bicarbonate were always well charged with carbon dioxide and were tested for hydroxyl with phenolphthaleine before being used in culture experiments, and again at the end of the experiment. It is quite possible, of course, that a small error was thus introduced, as the carbonic acid formed by the dilution of carbon dioxide in water may have retarded somewhat the dissociation or ionization of the sodium hydrogen carbonate. It is improbable that sodium hydrogen carbonate, unaccompanied by the normal carbonate, would ever occur in nature except in the presence of an excess of carbon dioxide, which fact is a further justification of the procedure here described.

In order to demonstrate that this excess of carbon dioxide was not in itself injurious to the roots of white lupine, the following simple check experiment was made: Carbon dioxide was forced into distilled water until a saturated solution was obtained. Plants were then entered in this solution, which was protected as completely from loss of carbon dioxide as circumstances would permit. After twenty-four hours the solution was tested with barium hydrate, and the heaviness of the resulting precipitate of barium carbonate showed that very much more carbon dioxide still remained than is present in ordinary water. During this period the roots grew nearly as well as in water containing only the normal quantity of carbon dioxide. It might be supposed that a solution of carbon dioxide in water and presumably containing the hypothetical carbonic acid must needs be itself quite toxic, as it would be expected to yield the hydrogen ion which recent investigations have shown to be excessively toxic. In this connection some work of Pfeiffer [Ann. Chem. (2), 23, 625 (1884)] will prove interesting. This investigation showed that a solution of carbon dioxide is an exceedingly poor conductor; that in fact the highest conductivity observed in such solutions was only about a thousandth of that which Kohlrausch's work showed it should possess. See also Knox [Ann. Phys. Chem., 54, 44 (1895)] and Walker and Cormack [Journ. Chem. Soc., 77, 5 (1900)].

It would seem rational, therefore, to consider that carbonic acid does not exist itself, or at least in only minute quantities in solutions of carbon dioxide, but is *potentially* present in its constituents and only forms in the presence of some added influence, such as a base. And that, therefore, even a concentrated aqueous solution of carbon dioxide would contain no hydrogen ions, or so very small a quantity as to be ineffective against so delicate an indicator as a plant root.

Experiments to ascertain the limit of endurance in pure solutions were also made with seedlings of alfalfa (*Medicago sativa*). Although absolute limits for this plant have not, as yet, been determined, they appear to be somewhat lower for every salt than in the case of *Lupinus albus*, but more than one-half as high. Thus for magnesium sulphate the limit appears to lie between 0.000625 and 0.00125 normal, while for magnesium chloride the limit will be found between 0.00125 and 0.0025 normal.

A glance at the preceding table shows very clearly that it is the basic rather than the acid radicle of the salts used which chiefly determines their relative toxicity. In other words, the cations derived from these salts are very much more active in their effect upon plant tissues than are the anions. This is strikingly brought out by a comparison among themselves of the three chlorides of magnesium, sodium, and calcium, on the one hand, and of the chlorides and sulphates of magnesium and sodium, respectively, on the other. In the former case, although the anions (Cl) are identical in kind we find magnesium chloride eight times as toxic as sodium chloride, and one hundred times as toxic as calcium chloride. In the latter case, magnesium sulphate is only twice as toxic as magnesium chloride, while sodium sulphate is little more than two and one-half times as injurious as the corresponding chloride.

The results with salts of magnesium, as compared with those of sodium, confirm the results obtained by W. Wolf, Loew, and others as to the strongly poisonous qualities of the former base.

All four of the salts of sodium with which experiments were made are widely distributed and often very abundant in the alkali regions of the western United States. As was to be expected, sodium carbonate or black alkali was found to be the most harmful of these, but it is not much more injurious than sodium sulphate. That the latter is much more poisonous than sodium chloride is a result not altogether anticipated at the beginning of the investigation.<sup>1</sup> As was predicted, sodium bicarbonate proved to be somewhat less toxic than sodium chloride.<sup>2</sup>

As a matter of fact, the limit of endurance in a solution of sodium bicarbonate is not much higher in parts of salt per 100,000 of water

<sup>1</sup>Stewart [Ninth Ann. Rep. Utah Agr. Exp. Sta. p. 26 (1898)] found sodium chloride more injurious than sodium sulphate to germinating seeds of legumes and cereals.

<sup>2</sup>Very different results from these here recorded as to the relative toxicity of the carbonate and bicarbonate of sodium were obtained by Coupin [Rév. Gén. de Botanique, 12, f80 (1900)]. Experimenting with seedlings of wheat, this author found that the least concentrated fatal solution ("équivalent toxique") is 1.1 grams per 100 of water for sodium carbonate, while for the bicarbonate it is 0.6 gram. Hence the latter would be twice instead of one-fourth as poisonous as the former. Sigmund [Landw. Versuchsst., 47, 2 (1896)] found that while  $\text{Na}_2\text{CO}_3$  at a concentration of 0.5 per cent killed germinating seedlings of vetch and rape and retarded the development of wheat seedlings,  $\text{NaHCO}_3$  at the same concentration was harmless.

and is no higher in fractions of the reacting weight than it is for sodium chloride. It should be mentioned, however, that the plants survive in a solution of the bicarbonate of the strength given in the table in much better condition than in the corresponding concentration of the chloride, so that the latter must be regarded as the more harmful of the two salts. The wide distribution of sodium bicarbonate and its abundance as a component of many alkali soils renders the demonstration of its marked poisonous effects upon vegetation, even when present in comparatively dilute solutions, a matter of no little importance. Although much less injurious than is the normal carbonate or "black alkali," the presence of this salt can not be neglected in future estimations of the value of western soils.

An explanation of the harmful action of sodium bicarbonate which at first suggested itself was that by its dissociation free hydrogen ions are liberated, though the weight of evidence on chemical grounds is rather against this view.<sup>1</sup> It has been shown by recent investigators<sup>2</sup> that it is probably the hydrogen ions dissociated by certain acids (especially the strong mineral acids) which make them so injurious to organisms, even in extremely dilute solutions. If this were the reason for the toxicity of sodium bicarbonate it would follow that water heavily charged with carbon dioxide, as in the check experiment described above (p. 20), would prove similarly injurious to plant roots by reason of the dissociation of hydrogen ions by the carbonic acid ( $\text{HCO}_3$ ), which is supposed to be formed when carbon dioxide is dissolved in water. But, as has already been noted, no toxic effect was obtained with an aqueous solution of carbon dioxide.<sup>3</sup>

<sup>1</sup> Walker and Cormack, Journ. Chem. Soc., 47, 5 (1900) and Bodländer, Zeit. für physik. Chem., 35, 25 (1900).

<sup>2</sup> Kahlenberg and True, Bot. Gazette, 22, 87 (1896); Heald, l. c., p. 134; Loeb, Pflüger's Archiv f. die gesammte Physiologie, 69, 4 to 9 (1898); Kahlenberg and Austin, Journ. of Physical Chem., 4, 553 (1900); True, Amer. Journ. Sci. ser. 4, 9, 183 (1900).

<sup>3</sup> There exists among plant physiologists some diversity of opinion as to the direct effect of large quantities of carbon dioxide upon the growth of roots. The subject is evidently one which needs a more thoroughgoing investigation, not only from a scientific standpoint, but from economic reasons also, as it is intimately connected with tillage and drainage problems. For an extended discussion of this question see Lopriore in Jahrb. für wiss. Botanik, 28, 531 (1895). The author mentions that Boehm found roots of the bean (*Phaseolus vulgaris*), when exposed to an excess of carbon dioxide, to be shorter, and the lateral roots fewer, than is ordinarily the case. Jentys [Bul. Internat. Acad. Sci. Cracovie, 1892, 306 (1893)], found that by passing atmospheric air to which had been added 4 to 12 per cent of carbon dioxide through the soil of culture pots, an injurious effect upon the roots of the bean and the yellow lupine could be detected, although the injury was less than in Boehm's experiments. On the other hand, wheat was practically unharmed. Lopriore (l. c., p. 623), concludes that carbon dioxide in excess has a hindering but not a permanently injurious influence upon the functions of protoplasm. This effect is not ascribable to the absence of oxygen, but is specific. Plant cells can gradually accommodate themselves to a quantity of carbon dioxide, which, if applied directly, would injure them. Lopriore's experiments were made chiefly with *Mucor*, yeast, and pollen grains and tubes.

As there is probably but a small difference in the amount of sodium ions yielded by sodium chloride and by sodium hydrogen carbonate, at the dilutions here involved, the difference in their toxicity observed must in all probability be ascribed mainly to the anions.

It is likely that the great toxicity of normal sodium carbonate is largely due to the hydroxyl ions resulting from the hydrolysis of this salt. In the case of the bicarbonate of sodium in all the experiments involving its use, and described in this paper, hydrolysis was avoided by dissolving carbon dioxide in the solution in amounts sufficient to prevent any inversion to the normal carbonate, a reaction which would necessarily result were hydrolysis of the bicarbonate permitted.<sup>1</sup> Since it seems reasonably certain that  $\text{HCO}_3$  ions are not toxic, the toxic influence of the sodium bicarbonate solutions could be safely attributed to the sodium ion alone were it not for the fact that toxic solutions of this salt produce the peculiar "clearing" effect upon plant tissues which is well known in the case of the normal carbonate of sodium and of the hydrates of potassium and of sodium. This effect is very different from that caused by other salts of sodium, e. g., the sulphate and the chloride.

Calcium chloride was found to be ten times less injurious than is sodium chloride. For this reason, and because it rarely predominates in areas of any considerable size, this salt can not be regarded as, under ordinary circumstances, a dangerous component of alkali soils. As we shall presently see, there is reason to believe that it can in many cases be a highly beneficial component of the soil.

Attention should be directed to the fact that the figures given in the above table represent only approximate results, the determination of the absolute limit for each salt depending theoretically upon the testing of an almost infinite number of concentrations. Thus, as a rule, solutions of a concentration of 0.2, 0.15, 0.1, 0.075, 0.050, etc., normal were employed, although more numerous intermediate concentrations, e. g., of 0.2000, 0.1825, 0.1750, etc., normal could have been tested. However, it is doubtful whether the reaction upon plant tissues of finer differences could be detected, and it is believed that for all practical purposes a sufficient number of concentrations was used. As has already been noted, the limits of endurance in the case of different salts are not of precisely equal value, the roots not surviving in all in exactly the same condition. Thus roots which survived after twenty-four hours in a 0.005 normal solution of sodium carbonate presented a perfect appearance and grew vigorously in distilled water during a subsequent period of twenty-four hours. On the other hand, roots which endured a 0.25 normal solution of calcium chloride presented a markedly abnormal aspect at the end of twenty-four hours, and made little subsequent growth when transferred to water. Likewise

<sup>1</sup>See paper on Equilibrium between Normal Carbonates and Bicarbonates in Aqueous Solutions, Cameron and Briggs. Bul. 18, Div. Soils, U. S. Department of Agriculture (1901); Jour. Physical Chem., 5, 537 (1901).

roots survived in better condition in 0.0075 normal sodium sulphate than in 0.02 normal sodium chloride solution. It was found much easier to determine sharply the limit of endurance for sodium carbonate and sodium bicarbonate than for other salts, as in 0.005 and 0.02 normal solutions of the two carbonates, respectively, all, or nearly all, roots survived in apparently perfect condition, while in 0.0075 and 0.025 normal, respectively, all roots were killed and symptoms of advanced disorganization were apparent after twenty-four hours.

CONCENTRATION MINIMUM PROHIBITING ELONGATION OF ROOTS.

A comparison of the seven salts above enumerated in regard to the degree of concentration of each in which absolutely no elongation of the roots occurred during twenty-four hours is interesting, as illustrating how far this point is removed from that of the minimum concentration which is still toxic. It will be seen that the position of the salts in this scale does not at all correspond with their sequence in the table of limits of endurance. In many cases, especially when the solution was still more concentrated, not only no increase of length but a positive shrinkage of 0.5 to 2 mm.<sup>1</sup> was detected.

TABLE II.—Concentrations which absolutely prevent growth.

Name of salt.	Concentration of solution.	
	Parts per 100,000 of solution.	Normal.
Sodium carbonate .....	260	0.05
Sodium bicarbonate .....	417	.05
Magnesium chloride .....	960	.2
Sodium chloride <i>a</i> .....	1,160	.2
Sodium sulphate .....	1,410	.2
Calcium chloride .....	1,652	.3
Magnesium sulphate .....	1,680	.3

*a* According to Pfeffer (*Pflanzenphysiologie*, Ed. 2, 1, 414) a culture solution to which enough potassium nitrate or sodium chloride is added to render it isosmotic with a 2 per cent potassium nitrate or 1.7 per cent sodium chloride solution causes a cessation of growth in ordinary plants while an increase to 3 per cent is necessary to prevent growth in halophytes.

It is impossible to reconcile this sequence, as compared with that of Table I, with the notion, which still appears to find advocates, that the injurious effect of these salt solutions is merely a function of their osmotic pressures. If any fresh evidence were needed to disprove this assumption it is afforded by the fact, very clearly brought out in the present investigations, that marked toxic effects frequently appear long before loss of turgor has manifested itself or cessation of growth has occurred. It is certain that no useful conclusions as to the degree of toxicity of a solution can be drawn from its osmotic pressure.

True [*Bot. Gazette*, 26, 407 (1898)] calls attention to the difficulty of distinguishing the purely chemical from the merely osmotic (plasma-

<sup>1</sup> In some solutions this loss of length due to plasmolysis was as great as that found by Sachs in roots which were exposed for thirty minutes to the dry air of a room. (*Arb. bot. Inst. Würzburg*, 1, 396; *Gesammelte Abhandl.*, 2, 784, 785.)

lyzing) effect of a salt solution. He experimented with *Spirogyra* in order to obtain means of making such distinction, comparing its behavior in a solution of cane sugar, which is believed to possess no chemically toxic properties, with that in solutions of sodium chloride and potassium nitrate. The maximum concentration of the sugar solution in which life could be maintained was determined to be 0.75 normal. Allowing for differences of dissociation, 0.46 normal should then be the maximum endurable concentration of a sodium chloride solution if only its osmotic pressure were involved. In fact, however, 0.1 normal was found to be the actual limit, so that a definite toxic action of sodium chloride must be admitted (*loc. cit.*, p. 410).<sup>1</sup>

Were the injurious action of these solutions attributable to plasmolysis alone, an approximately equal amount of elongation should take place in solutions of different salts, if each solution contain an equal fraction of a gram equivalent to a given amount of water, granting that the dissociation of each salt was equally great at the given concentration, as would be approximately true for strong electrolytes at the concentrations here used; for elongation and growth in general are intimately connected with the turgor conditions of the tissues,<sup>2</sup> which, in turn, depend upon the osmotic force exerted by the surrounding solution. That force being equal for each of two solutions, the turgor and the amount of elongation of the roots immersed in each should also be equal if osmosis were the only factor involved. That this is not the case is sufficiently established by the figures given in Table II.

#### RESULTS WITH LESS SOLUBLE SALTS.

Besides the easily soluble alkali salts a few others were used in experiments, i. e., calcium sulphate [ $\text{CaSO}_4$ ], calcium carbonate [ $\text{CaCO}_3$ ], calcium bicarbonate [ $\text{Ca}(\text{HCO}_3)_2$ ], and the carbonate and bicarbonate of magnesium [ $\text{MgCO}_3$  and  $\text{Mg}(\text{HCO}_3)_2$ ]. These were found to be either toxic in a very slight degree, indifferent, or positively stimulating to growth.

<sup>1</sup> From True's results it is clear that at the concentrations involved in our experiments with pure solutions the toxic effect observed must in every case be referred to action of a chemical rather than a purely physical nature. In some of the mixed solutions, such as the very concentrated ones containing calcium sulphate, it may be that their osmotic pressure determines the limit of endurance of the plant roots.

<sup>2</sup> For example that, except perhaps in rare instances, growth can not be resumed after an interruption (such as is occasioned by transference of plants from one medium to another) unless the turgor of the plant or the organ concerned is nearly or quite normal, was shown by Curtis [*Bul. Torr. Bot. Club*, 27, 1 (1900)] in the case of mycelia of *Mucor*, *Botrytis*, and *Penicillium*, grown in a plasmolyzing solution (4 per cent potassium nitrate). As this author expresses it, "there is a necessity of a certain turgor force before growth is possible, and growth can not occur until a turgor pressure has been reached which is normal to the plant growing in the given solution." (*Loc. cit.*, p. 11.)

In a (necessarily dilute) solution of gypsum, which contained a considerable quantity of the undissolved salt in suspension, the plants grew decidedly more vigorously than in pure water.<sup>1</sup>

In a saturated, but necessarily very dilute, solution of normal calcium carbonate [ $\text{CaCO}_3$ ], roots of *Lupinus* elongated nearly twice as much and remained in decidedly better condition during twenty-four hours than in distilled water. This solution gave a faint reaction for hydroxyl (with phenolphthaleine) at the beginning of the experiment, but none at the end of twenty-four hours, doubtless because of the production of carbonic acid through the excretion of carbon dioxide by the roots. But a solution of calcium bicarbonate [ $\text{Ca}(\text{HCO}_3)_2$ ], made by saturating a portion of the same calcium carbonate solution with carbon dioxide, permitted only about one-third as much growth of the roots as took place in distilled water. Their condition was decidedly abnormal at the end of twenty-four hours, even the turgor being poor.<sup>2</sup>

Magnesium carbonate [ $\text{MgCO}_3$ ], in a solution which gave a strong hydroxyl reaction with phenolphthaleine, allowed the roots to grow about as rapidly as in distilled water and to remain in about normal condition. On the other hand, a portion of the same solution to which an excess of carbon dioxide was added and in which no free hydroxyl could be detected (either before or after the experiment) exerted a strongly toxic action upon the roots. These made practically no growth during twenty-four hours; their turgor became decidedly inferior, and there occurred a marked discoloration of brownish spots, such as is produced by the readily soluble magnesium salts. Here it is obviously a case of a greater amount of magnesium in solution, owing to the presence of carbon dioxide in

<sup>1</sup> The stimulating effect which lime often exercises upon the growth of plants is too well known to require illustration. The presence of calcium salts in considerable quantity leads to a more vigorous production of root hairs than is normally the case, as can easily be demonstrated by culture experiments, in which only the tip of the root is immersed in the calcium salt solution. On the surface of the root above the solution a great number of unusually long root hairs appear. To this effect of the presence of lime, and the consequent readier absorption of potassium and ammonium salts from the soil, Loew attributes in part the benefits obtained by liming. (Bul. No. 18, Div. Veg. Phys. and Path., U.S. Department of Agriculture, p. 43.) That calcium salts directly stimulate growth, apart from the production of root hairs, is, however, shown by cultures with the root entirely immersed in an aqueous solution, thus precluding any important development of these organs.

<sup>2</sup> Schloesing's investigations [Comptes rendus. 74, 1552 (1872)] showed that 100,000 parts of pure water, i. e., free from dissolved carbon dioxide, would dissolve about 1.3 parts of calcium carbonate. Treadwell and Reuter [Zeit. für anorg. Chem., 35, 28 (1900)] showed that by increasing the pressure of the carbon dioxide in the gas phase in contact with the solution until it was one atmosphere, the solubility was increased so that 100,000 parts of water would dissolve 116 parts of calcium carbonate. Even at this extreme solubility there would be but 46 parts of calcium per 100,000 of water, as against about 60 parts in a saturated solution of calcium sulphate, in which plants thrive well.



excess.<sup>1</sup> Why the corresponding calcium solution should also hinder growth can not be satisfactorily explained at present.

#### RESULTS WITH MIXED SOLUTIONS.

Upon comparing the limits of endurance for lupine roots in pure solutions of the "alkali" salts with the limits determined by the methods employed in a field survey, it became obvious that the former were vastly lower than the latter; and that furthermore the order of toxicity of the several salts as fixed by investigators in the field differed greatly from that obtained by experiments in the laboratory. This was strikingly the case with magnesium sulphate, which is decidedly the most toxic of the seven salts when alone in a pure aqueous solution, but which is regarded as the least injurious by students of alkali soils. But it was recalled that none of these salts usually occurs in any notable quantity in the soil save in the presence of one or several others, both of the readily soluble salts and of the comparatively insoluble magnesium carbonate, calcium carbonate, and calcium sulphate. The key to the discrepancy appeared therefore to lie in mixtures of the various salts, and the study of these became, logically, the next step in the investigation.

In experimenting with mixed solutions it was planned to test every possible combination of two of the readily soluble salts with which experiments were made in pure solutions. Another line of experiments, from which were obtained results which are believed to be of considerable scientific interest and from an economic point of view to indicate one of the possible solutions of the alkali soil problem, consisted in combining each of the readily soluble salts with each of three difficultly soluble ones—calcium sulphate, calcium carbonate, and magnesium carbonate. The only triple mixtures so far tried are those of each readily soluble salt (except calcium chloride) with calcium sulphate and calcium carbonate. Sodium bicarbonate was tested only in this triple mixture.

Although the work with mixtures of salts is by no means com-

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<sup>1</sup> Treadwell and Reuter [*Zeit. für anorg. Chem.*, **17**, 199 (1898)] showed that at 15° C. and under a partial pressure of carbon dioxide in the vapor phase equal to zero, pure water dissolves about 63 parts of magnesium carbonate per 100,000. With a partial pressure of carbon dioxide in the vapor phase equal to one atmosphere there was dissolved about 1,211 parts magnesium hydrogen carbonate, equivalent to 698 parts of the normal carbonate per 100,000 of solution. It is thus seen that the solubility is enormously increased by the presence of carbon dioxide. Cameron and Briggs [*Bul.* 18, p. 22, Division of Soils, U. S. Department of Agriculture (1900)] showed that a solution of magnesium carbonate in solution in equilibrium with ordinary air contained about 18 parts of magnesium in 100,000 of solution, which might have been expected to be enough to prohibit growth in view of the toxicity of solutions of magnesium chloride and magnesium sulphate. It should be further noted that it was shown that 6 parts of the dissolved magnesium was combined as the normal carbonate, so that the solution contained more than appreciable amounts of OH ions, resulting from the hydrolysis of this latter salt.

pleted, the data thus far obtained throw so much light on the whole subject of alkali soils, and go so far to account for the fact that the limits of endurance of plants in pure solutions of the various salts are low as compared with those determined from the observations of survey parties in the field, that it seems advisable to present them here.

In the case of mixtures of two readily soluble salts, solutions of each, of twice the desired concentration, were mixed in equal volumes. Where one of the salts is a comparatively insoluble one, it was added in solid form to a solution of definite concentration of the soluble one, and the mixture was then diluted to the required concentration, as though the more soluble salt alone were present. (The source of error incurred by this method was considered so slight as to be practically negligible.) The mixture was then allowed to stand for a week or ten days with frequent shaking, in order to bring it to equilibrium before using. In all mixtures of magnesium carbonate and of calcium carbonate alone with other salts, the undissolved residue was removed by filtration. Likewise in earlier experiments with calcium sulphate added to other salts, the residue was removed, but in those upon which are based the limits given in the tables it was retained. In all cases where both calcium sulphate and calcium carbonate were added, the undissolved residue remained during the culture. The difference in limit due to the presence or absence of a solid excess was, however, usually imperceptible, and always slight.

In every case the object was to ascertain how far the limit of endurance for the roots in the presence of the more toxic salt could be raised by addition of one that is less injurious. Although the concentration of solution of the latter is invariably stated, if it be a readily soluble salt, it is the concentration of solution of the more poisonous salt as denoting a corresponding limit of endurance to which attention is chiefly directed. It is interesting that in cases where both of the salts mixed are readily soluble ones the less toxic salt appears usually to be more effective in neutralizing the more toxic one when added in concentration somewhat above rather than below that in which plant roots will endure it when alone. Thus, in a mixture containing equal volumes of 0.0075 normal sodium carbonate and 0.01 normal sodium sulphate, roots of two plants survived, but all died when the mixture contained 0.0075 normal sodium carbonate and only 0.005 normal sodium sulphate. Also a majority of the roots could retain their vitality in a mixture containing equal volumes of 0.0025 normal magnesium sulphate and of 0.01 normal sodium sulphate, but not in 0.0025 normal magnesium sulphate plus 0.005 normal sodium sulphate. Similar results were obtained by adding sodium sulphate to magnesium chloride and sodium chloride to magnesium sulphate. The reverse was true, however, in the mixtures of magnesium chloride and sodium chloride, the less concentrated solution of the latter proving more beneficial.

The concentrations are stated, as in preceding tables, both in parts of salt to 100,000 of solution and in fractions of a normal solution.

In the following tables of the effects of mixtures each of the more soluble alkali salts (excepting sodium bicarbonate) is taken up in succession in the order of its toxicity in pure solution. The neutralizing effect is expressed in terms of the greatest concentration of the more toxic salt endurable in the presence of the less toxic one. As the determination of the value of a less injurious salt in neutralizing a more toxic one was the objective of all experiments with mixtures, it follows that the number of added salts decreases successively from table to table. For comparison, the limit of endurance for the more toxic salt in pure solution is stated at the head of the table. The details of neutralizing effect upon each salt are taken up in connection with its respective table, while a discussion of the general significance of the whole series of experiments with mixtures of two solutions is appended.

The results embodied in Tables III to IX were obtained from experiments with *Lupinus albus* only. In Table X, however, the limits are given for both *Lupinus albus* and *Medicago sativa* (alfalfa) in solutions of each readily soluble salt (excepting calcium chloride) in the presence of an excess of calcium sulphate and calcium carbonate together.

#### MAGNESIUM SULPHATE IN MIXTURES.

The following table shows the results of experiments with *Lupinus* in solutions of magnesium sulphate with other salts added:

TABLE III.—*Limits for magnesium sulphate in mixtures.*

Name of salt added.	Greatest endurable concentration of magnesium sulphate.		Concentration of the salts added.	
	In fractions of a normal solution.	In parts per 100,000 of solution.	In fractions of a normal solution.	In parts per 100,000 of solution.
None	0.00125	7		
Magnesium chloride	.000625	3.5	0.0025	12
Sodium carbonate	.00125	7	.0025	13
Sodium sulphate	.00375	21	.01	80
Sodium chloride	.0075	42	.015	87
Calcium chloride	.2	1,120	.2	1,101
Magnesium carbonate	.01	56	Saturated.	Saturated.
Calcium carbonate	.02	112	Saturated.	Saturated.
Calcium sulphate	.6	3,360	Saturated.	Saturated.
Calcium sulphate and calcium carbonate	.4	2,240	Saturated.	Saturated.

In the light of figures given above, the enormous discrepancy between the results obtained by experiments with this salt in pure solution and the limit determined by field survey is completely obliterated. For in alkali lands magnesium sulphate is rarely, if ever, found in any quantity except in the presence of calcium sulphate; and it is commonly accompanied by both sodium and calcium sulphate (the Billings,

Mont., type of alkali soil<sup>1</sup>). Addition of sodium sulphate, which is itself so injurious in a pure solution, raises the limit for magnesium sulphate three times, while the presence of calcium sulphate allows a small proportion of the roots to barely survive during twenty-four hours in a solution of magnesium sulphate 480 times as concentrated as that which, in pure solution, represents the limit of endurance. A careful comparison was made between 0.3 and 0.4 normal solutions of magnesium sulphate, both in the absence and the presence of an excess of calcium sulphate, five individuals of *Lupinus albus* being cultivated for 48 hours in each of the four solutions. The following table gives the results:

TABLE IV.—*Magnesium sulphate with and without calcium sulphate.*

Solutions.	Average elongation of the marked portion of the root.	General condition of the roots.
	<i>Millimeters.</i>	
Magnesium sulphate (0.3 normal) -----	0.7	Extremely flaccid, and discolored with brownish blotches; extremely plasmolyzed.
Magnesium sulphate (0.3 normal) + calcium sulphate.	10.2	Turgor normal; plasmolysis none; but all roots quite badly discolored.
Magnesium sulphate (0.4 normal) -----	.3	About as in 0.3 normal.
Magnesium sulphate (0.4 normal) + calcium sulphate.	13.0	Turgor normal; plasmolysis none; all but one root quite badly discolored.

In both pure solutions the protoplasm of the nearly isodiametric cells of the periblem was completely withdrawn from the cell wall and collected with the nucleus in a compact mass near the center of the cell; while in both solutions to which calcium sulphate had been added no trace of plasmolyzing action could be detected in the cells of the periblem, the protoplasm being closely applied to the wall, with large vacuoles in the older cells, and the nucleus usually peripheral. Precautions were taken while preparing the sections to keep the tissues immersed in the culture solution, and the absence of plasmolysis in the roots taken from the solutions containing calcium sulphate is sufficient evidence that the pure solutions had produced this effect during the period of culture rather than after withdrawal.<sup>2</sup>

<sup>1</sup> See Whitney and Means, Bul. 14, Div. Soils, U. S. Department of Agriculture (1898), and Cameron, Bul. 17, p. 32, Div. Soils, U. S. Department of Agriculture (1901).

<sup>2</sup> Wolf's observation (see footnote, p. 40) that both  $\text{Ca}(\text{NO}_3)_2$  and  $\text{Mg}(\text{NO}_3)_2$  are readily absorbed by plant roots when mixed together, while neither is readily absorbed from a pure solution, renders it highly probable that in this case of a mixture of  $\text{MgSO}_4$  and  $\text{CaSO}_4$  it is the rapid endosmosis of the salts into the cells of the plant roots which prevents plasmolysis of the latter. In short this mixture is to be compared with those substances described by Overton [Vierteljahrsschr. Naturf. Gessellsch. Zürich 40, 1 (1895)] which produce only transient plasmolysis, owing to their more or less rapid passage through the ectoplasm into the cell sap. As determined by De Vries [Jahrb. für wiss. Botanik, 14, 537 (1884)], a 1.8 per cent solution of magnesium sulphate (which would correspond to our 0.3 normal

In the presence of both calcium sulphate and calcium carbonate added in excess to a solution of magnesium sulphate, the limit of endurance is only two-thirds as high as when calcium sulphate alone is added.

Calcium as the chloride has also a powerful effect in neutralizing the toxicity of magnesium sulphate. But here the addition of a new anion (Cl), besides the added cation (Ca), seems to diminish the beneficial effect of the latter, since the chloride, although a readily soluble salt, raises the limit for magnesium sulphate only one-third as much as does the little-soluble calcium sulphate. In a mixture of calcium chloride and magnesium sulphate a crystalline precipitate of calcium sulphate separates slowly or rapidly in proportion to the concentration of the solutions, so that the case becomes that of the contact of solid calcium sulphate with a solution of magnesium chloride. As would be expected, the limit of endurance for magnesium sulphate plus calcium chloride is the same as that for magnesium chloride plus calcium sulphate (Table V).

Sodium salts are very much less effective in neutralizing magnesium sulphate than are salts of calcium. In the case of sodium salts it is the chloride which is most effective, so that here we seem to have a beneficial effect of the anion as well as of the cation. Yet the absence of any neutralizing effect when magnesium chloride is added to magnesium sulphate shows that the Cl ions alone are ineffective.

In one case the addition of a salt with a common basic ion—i. e., magnesium carbonate—raises the limit of endurance in magnesium sulphate eight times.<sup>1</sup> By a simple process of elimination, since magnesium ions are ineffective in the form of magnesium chloride when added to magnesium sulphate, although chlorine ions appear to have in themselves some neutralizing value when added as sodium chloride, we are compelled to attribute the beneficial influence of magnesium carbonate to  $\text{CO}_3$ , or more probably  $\text{HCO}_3$ , ions, a point to which we will return in discussing the stimulating effect of dilute solutions of sodium carbonate and sodium bicarbonate. Noteworthy is the fact that calcium carbonate, although much less soluble than the corresponding salt of magnesium, is twice as effective an antidote for magnesium sulphate. This affords another striking proof of the great efficacy of calcium as a remedy for magnesium poisoning.

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solution), is the isotonic equivalent of a 0.1 normal solution of potassium nitrate, which is usually taken as the unit in measurements of osmotic pressure of solutions. True [Bot. Gazette, 26, p. 410 (1896)] found that plasmolysis of Spirogyra cells in a  $\text{KNO}_3$  solution first appeared at a concentration of 0.25 normal. De Vries' results seem to indicate that the osmotic value of each component in a mixed solution (of two or three salts) is equal to that of the respective component when present alone at the given concentration, a point not in accord with well-established facts.

<sup>1</sup>The roots barely survive in poor condition in a 0.01 normal magnesium sulphate solution plus an excess of magnesium carbonate; but in 0.005 normal magnesium sulphate solution plus magnesium carbonate some of the roots were perfectly normal after a twenty-four hours' culture.

## MAGNESIUM CHLORIDE IN MIXTURES.

The results of experiments with magnesium chloride in mixtures with other salts are shown in the following table:

TABLE V.—*Limits for magnesium chloride in mixtures.*

Name of salt added.	Greatest endurable concentration of magnesium chloride.		Concentration of the salts added.	
	In fractions of a normal solution.	In parts per 100,000 of solution.	In fractions of a normal solution.	In parts per 100,000 of solution.
None .....	0.0025	12		
Sodium carbonate .....	.0025	12	0.00375	19.5
Sodium sulphate .....	.01	48	.01	80
Sodium chloride .....	.01	48	.02	116
Calcium chloride .....	.1	480	.15	726
Magnesium carbonate .....	.0025	12	Saturated.	Saturated.
Calcium carbonate .....	.04	192	Saturated.	Saturated.
Calcium sulphate .....	.2	960	Saturated.	Saturated.
Calcium sulphate and calcium carbonate .....	.2	960	Saturated.	Saturated.

In the alkali soils of the Western United States magnesium chloride rarely occurs in such large quantities as to be regarded as more than secondary in importance.<sup>1</sup>

As in the case of magnesium sulphate, calcium is found to be much more effective than sodium in neutralizing magnesium, but here calcium chloride is relatively more effective than with magnesium sulphate, raising the limit for magnesium chloride one-half (instead of only one-third) as far as does calcium sulphate. But calcium is much less effective with the chloride than with the sulphate of magnesium, as is evident from the relative efficacy of calcium sulphate in raising the limits of endurance of the two magnesium salts. Hence we have here another indication (as in the case of calcium chloride added to magnesium sulphate) that chlorine ions by their presence lower the neutralizing efficacy of calcium; although in the absence of the latter base, magnesium chloride is only one-half as toxic as is magnesium sulphate. While the beneficial effect of calcium sulphate upon magnesium sulphate is decreased by the addition of an excess of calcium carbonate, the presence of the carbonate does not affect the value of calcium sulphate as an antidote to magnesium chloride.

While calcium carbonate is equally effective in raising the limits of the two soluble magnesium salts (sixteen times), magnesium carbonate, which raised the limit of magnesium sulphate eight times,

<sup>1</sup> Magnesium rarely makes its specific effects upon plant life felt in the "alkali" soils, owing to the omnipresence there of considerable calcium salts. In certain areas of the Eastern States, notably in the so-called "serpentine barrens" of Pennsylvania and Maryland, it appears to be relatively more important, probably because it is there present in excess over calcium, although the actual amount of both, which may be present in the soil solutions at any given time, must be extremely small.

has no effect upon magnesium chloride. As it appears to be necessary to regard the  $\text{HCO}_3$  ions as the effective element in the former combination, we must conclude that these act beneficially in the presence of Mg and  $\text{SO}_4$ , but are powerless in the presence of Mg and Cl. But as calcium carbonate is equally effective as an antidote to magnesium chloride and to magnesium sulphate, it would follow that the power of Cl ions to hinder the effect of  $\text{HCO}_3$  ions disappears in the presence of Ca ions, while, as already noted, Cl ions appear to diminish the value of Ca ions as an agency for counteracting Mg ions. Comparisons such as these show how difficult it is to attempt an interpretation of toxicological phenomena in the light of current chemical and physiological ideas. Possibly determinations of the solubility and degree of dissociation of these different salts in mixtures may afford some clue to the numerous anomalies. On the other hand, it is difficult to see any justification for using the reactions of organisms in determining the dissociation constants of electrolytes. The many nonconcordant results recently described in the literature can hardly be regarded as throwing discredit upon the dissociation hypothesis, but rather as demonstrating the unsatisfactory nature of the method employed for the investigation in hand.

Sodium sulphate and sodium chloride are equally effective in raising the limit of magnesium chloride (four times). The former is more effective, and the latter decidedly less so, than in the case of magnesium sulphate, so that the anions (Cl,  $\text{SO}_4$ ) and not alone the cations (Mg, Na) appear to make their influence felt in these cases.

#### SODIUM CARBONATE IN MIXTURES.

Table VI shows results of experiments with mixtures of other salts with sodium carbonate:

TABLE VI.—*Limits for sodium carbonate in mixtures.*

Name of salt added.	Greatest endurable concentration of sodium carbonate.		Concentration of the salts added.	
	In fractions of a normal solution.	In parts per 100,000 solution.	In fractions of a normal solution.	In parts per 100,000 of solution.
None .....	0.005	26	.....	.....
Sodium sulphate .....	.0075	39	0.01	80
Sodium chloride .....	.0025	13	.01	58
Calcium chloride .....	.25	1,300	.25	1,377
Magnesium carbonate .....	.01	52	Saturated.	Saturated.
Calcium carbonate .....	.0075	39	Saturated.	Saturated.
Calcium sulphate .....	.03	156	Saturated.	Saturated.
Calcium sulphate and calcium carbonate .....	.03	156	Saturated.	Saturated.

As the above table shows, sodium chloride is ineffective as an antidote to sodium carbonate; calcium carbonate barely raises the limit

of endurance, while magnesium carbonate merely doubles it. It is interesting that magnesium carbonate should here be more effective than the corresponding salt of calcium, since in all other cases the latter is the more beneficial.<sup>1</sup> Sodium sulphate is likewise of very little neutralizing value, and the soluble salts of magnesium possess none so far as was ascertained. Calcium sulphate raises the limit only six times, the presence or absence of an excess of calcium carbonate not affecting the value of the sulphate. This comparatively slight efficacy of calcium sulphate in neutralizing "black alkali" is rather surprising in view of the accepted ideas of students of alkali soils in regard to the curative value of gypsum.<sup>2</sup> The comparative inefficacy of calcium sulphate in this case contrasts strikingly with its power to neutralize sodium in the forms of sulphate (Table VII) and chloride (Table VIII).

Calcium chloride is the only salt found to be very effective in neutralizing sodium carbonate, raising the limit of endurance for the latter fifty times. A mixture of solutions of the two salts causes an immediate heavy precipitate of calcium carbonate, to which fact the efficacy of the added salt must be largely ascribed. We should be dealing in this case with a solution of sodium chloride containing a large excess of calcium carbonate. Yet by direct addition of solid calcium carbonate to a solution of sodium chloride, the limit of endurance for the latter can be raised only three times, i. e., to 0.06 normal (see Table VIII). Here again chemistry appears to be powerless to afford an explanation of a phenomenon which, in the present state of our knowledge, must be regarded as paradoxical.<sup>3</sup>

A very noteworthy result was obtained by experiments with sodium carbonate, as well as with sodium bicarbonate, in the presence of an excess of calcium sulphate and calcium carbonate. In solutions of critical concentration of both of these mixtures a majority of the roots of the lupine plants were completely destroyed with pronounced

<sup>1</sup> The probability of the formation of a double carbonate, with a consequent lowering of the active mass, as well as a probable change of nature of the ions, suggests itself very forcibly in this connection. It is hoped that time and opportunity will be found in the near future to test this supposition in the laboratory.

<sup>2</sup> Hilgard, Bul. 128, Agr. Exp. Sta., Univ. Calif., pp. 16 to 18 (1900). It should be stated, however, that Hilgard recommends the application of gypsum under physical conditions which would not probably be considered analogous to those under which the experiments here described were performed.

<sup>3</sup> In marked contrast with this anomalous case is that of the mixture of magnesium sulphate and calcium chloride, in which a precipitate of calcium sulphate is formed and which is therefore to be regarded as a solution of magnesium chloride containing a solid excess of calcium sulphate. Here the limit of endurance is the same as when solid calcium sulphate is added directly to a solution of magnesium chloride. The same thing is true of a mixture of sodium sulphate and calcium chloride in which the limit of endurance is the same as for sodium chloride plus calcium sulphate.



corrosion due presumably to the action of hydroxyl ions, while a smaller number survived in apparently perfect condition, and this occurred in repeated experiments. In critical solutions of other salts and mixtures of salts, however, there was rarely such sharp difference in appearance between roots which survived and those which died during twenty-four hours' culture; as a rule none of the roots were in normal condition at the end of the experiment. In other words, the difference of individual plants in their power to resist toxic action appears to be more pronounced in the case of the two carbonates of sodium than of other "alkali salts." This would indicate that the selection of plants for resistance to "black alkali" offers a simpler problem than where resistance to other components of alkali soils is to be sought.

#### SODIUM SULPHATE IN MIXTURES.

Experiments with sodium sulphate in mixtures with other salts show the following results:

TABLE VII.—*Limits for sodium sulphate in mixtures.*

Name of salt added.	Greatest endurable concentration of sodium sulphate.		Concentration of the salts added.	
	In fractions of a normal solution.	In parts per 100,000 of solution.	In fractions of a normal solution.	In parts per 100,000 of solution.
None .....	0.0075	53		
Sodium chloride .....	.00375	26.5	0.01	58
Calcium chloride .....	.2	1,272	.2	1,102
Magnesium carbonate .....	.03	212	Saturated.	Saturated.
Calcium carbonate .....	.04	281	Saturated.	Saturated.
Calcium sulphate .....	.5	3,530	Saturated.	Saturated.
Calcium sulphate and calcium carbonate <i>a</i> .....	.3	1,908	Saturated.	Saturated.

*a* See Bul. 17., p. 22 et seq., Division of Soils, U. S. Department of Agriculture, 1901.

Sodium sulphate is very abundant in "alkali" soils, often occurring in contact with each or several of the other salts. In the Billings, Mont., type, for example, it is accompanied by the sulphates of magnesium and calcium, while in the Fresno, Cal., type it is in contact with sodium carbonate.

Most effective for neutralizing this salt is calcium sulphate, which raises the limit more than sixty times when added alone. In the presence of an excess of calcium carbonate, however, calcium sulphate can increase the limit of endurance for sodium sulphate only about forty times. This is probably due to a forcing back of the dissociation and decrease of solubility of the calcium sulphate by the calcium carbonate, although, as Cameron and Seidell<sup>1</sup> have shown, either salt is rather soluble in dilute solutions of sodium sulphate.

<sup>1</sup> Solution Studies of Salts Occurring in Alkali Soils, Bul. 18, Division of Soils, U. S. Department of Agriculture.

As in the case of all the other salts except sodium carbonate, calcium chloride is less effective than calcium sulphate, raising the limit only twenty-seven times. In this case, as in the mixture of calcium chloride with magnesium sulphate, a crystalline precipitate of calcium sulphate is formed, so that it actually becomes a case of the contact of calcium sulphate with a solution of sodium chloride, and the same limit was obtained by a direct test of this latter mixture. Calcium carbonate is much less effective in neutralizing sodium sulphate than in counteracting the toxic action of magnesium salts.

Calcium sulphate is more effective as an antidote to sodium sulphate than to any other salt tried except magnesium sulphate. In both these cases the anion of the added salt is the same as that of the more toxic one; hence the cathions alone seem to operate. Possibly a double salt of sodium and calcium is formed in this mixture. Since calcium sulphate is much less efficacious in neutralizing the chlorides of magnesium and sodium than the corresponding sulphates, while it is generally more beneficial than is calcium chloride, it seems almost certain that the beneficial action of Ca ions is in some way hindered by the presence of Cl ions. That Cl ions are in themselves less toxic than are  $\text{SO}_4$  ions would appear from the fact that the chlorides of magnesium and of sodium are less injurious in pure solution than are the corresponding sulphates.

#### SODIUM CHLORIDE IN MIXTURES.

Experiments with sodium chloride in mixtures with other salts yielded the results shown in the following table:

TABLE VIII.—*Limits for sodium chloride in mixtures.*

Name of salt added.	Greatest endurable concentration of sodium chloride.		Concentration of the salts added.	
	In fractions of a normal solution.	In parts per 100,000 of solution.	In fractions of a normal solution.	In parts per 100,000 of solution.
None .....	0.02	116		
Calcium chloride .....	.2	1,160	0.2	1,101
Magnesium carbonate .....	.04	232	Saturated.	Saturated.
Calcium carbonate .....	.06	348	Saturated.	Saturated.
Calcium sulphate .....	.2	1,160	Saturated.	Saturated.
Calcium sulphate and calcium carbonate .....	.2	1,160	Saturated.	Saturated.

Sodium chloride is probably the most widely distributed and generally abundant of the soluble components of alkali soils, occurring practically wherever the land is notably impregnated with these noxious salts.<sup>1</sup> As the above table shows, calcium sulphate and calcium chloride are equally effective in neutralizing the toxicity of sodium chloride, although in the case of sodium sulphate and the

<sup>1</sup> A notable exception is the Billings area in Montana.

soluble salts of magnesium, the former is decidedly more beneficial than the latter.

As in the case of magnesium chloride, the presence of calcium carbonate does not affect the neutralizing value of calcium sulphate, although decidedly diminishing it in the case of magnesium sulphate and sodium sulphate. It has been shown by Cameron and Seidell<sup>1</sup> that an excess of solid calcium carbonate has but a very slight effect on the solubility of calcium sulphate in sodium chloride solutions at the concentrations here involved. And from the general resemblance between the phenomena presented by calcium sulphate in contact with sodium chloride and magnesium chloride solutions, it is probable that calcium carbonate would have a like effect in the latter cases. It is to be regretted that laboratory investigations of the solubility of solid calcium carbonate and calcium sulphate in contact with solutions of soluble sulphates have not yet been made.

#### CALCIUM CHLORIDE IN MIXTURES.

In the experiments with calcium chloride in mixtures with other salts the following results were obtained:

TABLE IX.—*Limits for calcium chloride in mixtures.*

Name of salt added.	Greatest endurable concentration of calcium chloride.		Concentration of the salts added.	
	In fractions of a normal solution.	In parts per 100,000 of solution.	In fractions of a normal solution.	In parts per 100,000 of solution.
None.....	0.25	1,377		
Magnesium carbonate.....	.25	1,377	Saturated.	Saturated.
Calcium carbonate.....	.25	1,377	Saturated.	Saturated.
Calcium sulphate.....	a 0.3	1,652	Saturated.	Saturated.

a About.

Calcium chloride is quite generally distributed in alkali soils, being usually present in small patches wherever sodium chloride is abundant. As would be expected from the relatively very high concentration of the pure solution of this salt endured by roots of the white lupine, the limit can not be materially raised by the addition of other salts.

#### SODIUM BICARBONATE IN MIXTURES.

Sodium bicarbonate was tested in mixture only with calcium sulphate and calcium carbonate together, which raised its limit of endurance two and one-half times (see Table X). It usually occurs in nature in contact with the normal sodium carbonate.

#### CALCIUM SULPHATE AND CALCIUM CARBONATE IN MIXTURES.

In the tables of limits of endurance in mixtures, as in those of pure solutions, the figures do not perfectly state the case. For example,

<sup>1</sup> Bul. 18, Division of Soils, U. S. Department of Agriculture (1901).

although the limit of endurance in sodium carbonate plus magnesium carbonate is 0.01 normal, while for sodium sulphate plus magnesium carbonate it is 0.03 normal, the proportion of individual seedlings whose roots survive in good condition is decidedly greater in the latter mixture than in the former.

None of the readily soluble salts occurs abundantly in alkali soils save in the presence of calcium sulphate or calcium carbonate, and most often in contact with both. Hence it follows that the limits of endurance for the more soluble salts in the presence of these two salts of calcium, as obtained by means of water-culture experiments, should agree closely with the limits determined by soil investigators. This proved to be the case, due allowance being made for the influence of the physical properties of a soil as compared with an aqueous solution.

The following table serves to bring together, for ready comparison, the limit of endurance for roots of both white lupine and alfalfa in solutions of six of the easily soluble salts to which a solid excess of both calcium sulphate and calcium carbonate was added, the mixtures being brought to equilibrium before using.

TABLE X.—*Results with mixtures containing two calcium salts.*

Name of salt.	Limits for lupine ( <i>Lupinus albus</i> ).		Limits for alfalfa ( <i>Medicago sativa</i> ). <sup>a</sup>	
	Parts per 100,000 of solution.	Normal solution.	Parts per 100,000 of solution.	Normal solution.
Magnesium sulphate .....	2,240	0.4	1,960	0.35
Magnesium chloride .....	960	.2	960	.2
Sodium carbonate .....	156	.03	104	.02
Sodium sulphate .....	2,160	.3	2,160	.3
Sodium chloride .....	1,160	.2	1,160	.2
Sodium bicarbonate .....	417	.05	667	.08

<sup>a</sup> In the case of alfalfa a few roots barely survive in 0.55 and in 0.3 normal magnesium sulphate, while in 0.35 normal they make a noteworthy amount of growth during forty-eight hours. In 0.2 normal sodium sulphate they make a decidedly better growth, and in 0.1 normal sodium chloride two and one-half times as much growth as in the water control.

The close correspondence between the white lupine and alfalfa in their resistance to the effects of these mixed solutions is worthy of note, especially as alfalfa appears to be more sensitive than the lupine to pure solutions. The only serious discrepancy occurs in the mixture of sodium bicarbonate, calcium sulphate, and calcium carbonate, to which alfalfa roots appear to be nearly twice as resistant as are those of white lupine.

That in the neutralizing effect upon more toxic salts which these two relatively insoluble salts exert calcium sulphate plays a much more important part than does calcium carbonate is obvious from a comparison of the limits of endurance in solutions to which either calcium sulphate or calcium carbonate alone has been added. Indeed, in the case of magnesium sulphate and of sodium sulphate the limit of endurance is decidedly lower in the presence of both calcium salts

than when calcium sulphate alone is added. On the other hand, the presence or absence of calcium carbonate appears to have no effect upon the neutralizing value of calcium sulphate when added to magnesium chloride, sodium chloride, or sodium carbonate.

An interesting comparison is that of the soluble salts, one with another, in respect to their degree of toxicity in pure solution on the one hand, and in the presence of an excess of calcium sulphate and calcium carbonate on the other. It will be observed that the sequence in the first column is very different from that in the second. The most toxic salt or mixture is placed at the head of each column.

TABLE XI.—*Order of toxicity with and without calcium salts.*

In pure solution:	In presence of an excess of $\text{CaSO}_4$ and $\text{CaCO}_3$ : <i>a</i>
Magnesium sulphate.	Sodium carbonate.
Magnesium chloride.	Sodium bicarbonate.
Sodium carbonate.	Magnesium chloride. <i>b</i>
Sodium sulphate.	Sodium chloride <i>b</i>
Sodium chloride.	Calcium chloride.
Sodium bicarbonate.	Sodium sulphate.
Calcium chloride.	Magnesium sulphate.

*a* It has already been suggested that the limit in some of these highly concentrated solutions containing an excess of calcium salts may bear some relation to the osmotic pressure of the solution. It is therefore not a mere coincidence, perhaps, that the sequence in this column is almost identical with that in Table II (of concentrations precluding any growth during the culture).

*b* These two salts are equally toxic in mixtures if reacting weights be compared, while magnesium chloride is the more toxic of the two in parts of salt per 100,000 of solution.

The interest and importance of the results obtained from the experiments made with mixed solutions show the great desirability of extending further this line of investigation. In fact, no aspect of the work promises more substantial returns. An interesting problem among the many which suggest themselves in this connection is that of a possible relation between the degree of toxicity of a salt, alone or in mixture, and the readiness with which it is taken up by the plant from a solution. The occasion seems opportune to redirect attention to a series of experiments made long ago by Wilhelm Wolf<sup>1</sup> as to the

<sup>1</sup>Landw. Versuchsst., 7, 193 (1865). The studies were made with a series of solutions, each of which contained two salts in equal amount. Combinations were made with (1) salts of the same acid, but of different bases; (2) salts of the same base, but of different acids; (3) with both base and acid different. In each culture 200 c. c. of solution was employed, and after one-half of this volume had been absorbed by the plant (allowance being made for the small quantity of water evaporated directly from the solution) the amount of each salt taken up with the water was estimated by analysis of the residual 100 c. c. of solution. Young beans and maize were used in the experiments. Some of the results obtained were as follows:

From three mixtures, each containing 0.05 grams of each two salts, the plants absorbed in percentages of the original quantity of each salt supplied:

From ammonium nitrate plus calcium nitrate, 92 per cent of the former and 94 per cent of the latter.

From ammonium nitrate plus magnesium nitrate, 92 per cent of the former and 86 per cent of the latter.

From magnesium nitrate plus calcium nitrate, 74 per cent of each.

Potassium nitrate was taken up from all combinations with other nitrates

amount of each salt absorbed by a plant from a mixed solution. Especially interesting, as compared with the toxicological phenomena of pure and mixed solutions, respectively, are Wolf's results as to the effect of calcium sulphate in stimulating the absorption of other sulphates.

#### GENERAL SIGNIFICANCE OF RESULTS WITH MIXED SOLUTIONS.

To enter into a discussion, from the purely chemical point of view, of the widely accepted hypothesis of the dissociation of electrolytes in solution would be to exceed the proper limits of this paper.<sup>1</sup> It is sufficient to say that salts such as those with which we are here dealing are held to dissociate in dilute solutions, more or less com-

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(Na,  $\text{NH}_4$ , Mg, Ca) in absolutely greater amount than from a simple solution. From a solution containing 0.025 gram each of potassium nitrate and calcium nitrate the plants absorbed 100 per cent of the former and 88 per cent of the latter. From an equivalent solution of potassium nitrate plus magnesium nitrate, 100 per cent of the former and 88 per cent of the latter. The stimulation of the plant by the presence of calcium to take up greater quantities of potash is referred by Loew (l. c., p. 44) to the increased development of root hairs induced by the calcium. But if the presence of magnesium has exactly the same effect, as would appear from the experiment just quoted, we must look further for an explanation. Absorption of ammonium nitrate is decreased by the presence of other nitrates, *while that of calcium and of magnesium nitrates is stimulated thereby. It is remarkable that while neither of these last two salts is readily absorbed from a simple solution, both are easily absorbed when mixed together.*

Plants could be grown in mixtures of potassium and calcium sulphate ( $\text{K}_2\text{SO}_4 + \text{CaSO}_4$ ) and of calcium and magnesium sulphate ( $\text{CaSO}_4 + \text{MgSO}_4$ ), but never in mixtures of sulphates of potassium and sodium ( $\text{K}_2\text{SO}_4 + \text{Na}_2\text{SO}_4$ ), of potassium and ammonium ( $\text{K}_2\text{SO}_4 + (\text{NH}_4)_2\text{SO}_4$ ), nor of potassium and magnesium ( $\text{K}_2\text{SO}_4 + \text{MgSO}_4$ ), even when the solutions were very dilute.

Potassium and ammonium salts were taken up much more readily in the presence of a calcium salt than from a pure solution. This was notably the case with the sulphates, which are absorbed with difficulty from unmixed solutions. Gypsum (calcium sulphate) is absorbed in very small quantity in the presence of a potassium salt, but greatly stimulates absorption of the latter. From a mixture of calcium and magnesium sulphate little of either salt is taken up, but the presence of magnesium nitrate considerably increases the amount of calcium sulphate drawn from a solution.

From mixtures of a sulphate and a phosphate, the latter is always taken up in greater quantity. Magnesium sulphate is taken up in greater quantity in the presence of a phosphate than are other sulphates.

De Saussure's principle of the absorption of salts in solution by plant roots—i. e., that the salt is taken up in smaller proportion to the water absorbed than it occurs in the culture solution; in other words, that the residual solution becomes more concentrated—applies to the absorption of sodium chloride in the presence of a nitrate ( $\text{KNO}_3$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{Ca}(\text{NO}_3)_2$ ), but does not hold as to the absorption of the nitrate itself.

<sup>1</sup> For the presentation of the subject in simple terms the reader is referred to a former publication by one of us. (Rep. No. 64, U. S. Department of Agriculture, p. 144, 1900.)

pletely at a given concentration according to the specific properties of the particular salt. The result is a liberation of ions—atoms or atomic groups carrying or in some way associated with an electric charge. Cathions, those furnished by the basic radicle, carry positive electricity, while anions, derived from the acid radicle of the salt, are negatively charged. Ions possess a much greater velocity<sup>1</sup> than do undissociated molecules, and it is now believed by many physiologists that salts owe to the properties of their ions rather than to their entire molecules the toxic and other action which they exert upon organisms.<sup>2</sup>

It is believed that the results of the present investigation tend to confirm this view, although it must be admitted that serious anomalies exist, to some of which attention has already been directed.

Pure solutions of the salts dealt with are shown to be generally injurious to plants, and this largely by virtue of the cathions which they yield, as a comparison of the position of the several salts in the table of toxicity in pure solutions shows conclusively. Thus magnesium salts, irrespective of the character of their anions, are much more injurious than is any sodium salt, while the three chlorides (of magnesium, sodium, and calcium) differ enormously in toxicity, regardless of the fact that they yield a common anion.

An inspection of the tables of limits in mixed solution given above makes it clear that the addition of a second, less toxic salt in most cases increases the concentration of solution of the more harmful one in which root tips can retain their vitality. It is also demonstrated that addition of a second salt of the same base, hence furnishing a different kind of anion only, is usually much less efficacious in raising the limit than is the admixture of a salt of a different base. Thus magnesium chloride is ineffective as an antidote to magnesium sulphate, sodium chloride to sodium carbonate or to sodium sulphate, and calcium carbonate to calcium chloride.

If the assumption be granted that in the dilutions here involved the magnesium salts are practically completely dissociated and that the anions do not have a toxic effect, then a 0.00125 normal solution of magnesium will be the limit when the metal is combined as the sulphate and a 0.0025 normal solution when combined as the chloride, but about a 0.002 normal solution when both chloride and sulphate are present, with two equivalents of the former to one of the latter. The same line of reasoning holds for the other cases cited, and from these facts it is evident that the anions have a part in determining the toxic effect of a

<sup>1</sup>That the physiological action of ions may be in some sort a function of their specific velocities is indicated by Loeb's comparison of the effects of hydrogen and hydroxyl ions, as well as of various basic cathions, upon the absorption of water by a muscle. [Pflüger's Archiv., 69, 21, (1898).]

<sup>2</sup>Of a rapidly growing literature on this subject the papers of Kahlenberg and True and of Kahlenberg and Austin, dealing with plants, and those of Loeb, Garrey, Anne Moore, Kahlenberg, Clark and others, treating ion action upon animals, may be cited as of great importance. (See the Bibliography, p. 56.)

salt, although a much smaller one in general than have the cathions. Furthermore, these views are in harmony with Loeb's idea that  $\text{SO}_4$  ions are more toxic than Cl ions, because they tend to precipitate calcium from its proteid compounds.

In other cases, however, addition of a salt which furnishes new anions, but not new cathions, to the mixture is effective in raising the endurable limit of concentration for the more toxic salt. A striking case is the elevation of the limit for magnesium sulphate eight times by the addition of magnesium carbonate. Here it would appear that the  $\text{HCO}_3$  anions alone can be the effective agency. Sodium sulphate slightly raises the limit of sodium carbonate, and a relatively unimportant increase of the concentration of a calcium chloride solution in which lupine roots can survive is obtained by addition of calcium sulphate. But in these last two cases the effect is so small as to be almost negligible, and is perhaps entirely attributable to the forcing back of the dissociation of the more toxic salt rather than to any direct physiological action of the new anions.

The superior efficacy of cathions over anions in neutralizing the toxic effect of other cathions is illustrated by the discovery that sodium is equally effective as an antidote to magnesium chloride, whether it be added as sulphate ( $\text{Na}_2\text{SO}_4$ ) or as chloride ( $\text{NaCl}$ ).<sup>1</sup> A much more striking illustration is afforded by the fact that calcium, when added to a solution of magnesium sulphate or of sodium sulphate, is very much more efficacious when furnished as the relatively insoluble sulphate than as the readily soluble chloride. In other words, the presence of chlorine anions actually hinders the full exertion of the physiological effect of calcium cathions, unless we are to believe that the superior efficacy of calcium sulphate is due merely to its greater influence in retarding the dissociation of the sulphates of magnesium and of sodium.

If we turn now to the effect of mixtures in which two kinds of cathions are present we find that these are almost invariably much less poisonous than is the pure solution of the more toxic salt. Even the addition of a sodium salt (sulphate or chloride) to one of magnesium (sulphate or chloride) raises the limit of endurance for the latter three to six times. Still more remarkable is the effect of magnesium carbonate as an antidote to salts of sodium (carbonate, sulphate, chloride), raising their limits two to four times. But these effects are trivial as compared with the extraordinary efficacy of calcium in counteracting the toxic effects of other bases (magnesium, sodium).

Even when added as the but slightly soluble carbonate, calcium raises the limit of magnesium sulphate and of magnesium chloride sixteen times, of sodium sulphate more than five times, and of sodium

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<sup>1</sup> On the other hand, sodium chloride is twice as effective as sodium sulphate in neutralizing magnesium sulphate.



chloride three times. Calcium chloride<sup>1</sup> mixed with an equal volume of a magnesium or a sodium salt raises the limit of the latter as follows: Magnesium sulphate, one hundred and sixty times; magnesium chloride, forty times; sodium carbonate, fifty times;<sup>2</sup> sodium sulphate, twenty-seven times, and sodium chloride, ten times.

The most effective of the calcium salts tried was, however, calcium sulphate. This, when added alone in solid excess, increases the maxima of concentration endurable by the roots as follows: Magnesium sulphate, four hundred and eighty times; magnesium chloride, eighty times; sodium carbonate, six times; sodium sulphate, sixty-six times, and sodium chloride, ten times. Here we have probably the greatest effect of one kind of ion in neutralizing the effect of another kind that has yet been obtained in experiments with plants.

It is noteworthy that the effect of the calcium ions upon different salts having a common basic ion differs greatly. Thus plant roots can endure three times the concentration of a solution containing magnesium cations and sulph-anions to which calcium sulphate is added than they can of a solution containing magnesium cations and chlor-anions plus calcium sulphate. Yet the former solution in the absence of calcium salts is endurable in concentration only one-half as great as is the latter without a calcium salt. Here the effect may be partly due to differences of dissociation in the two solutions. But it appears necessary to attribute the greater part of it to an adverse influence, presumably exerted by chlorine ions, upon the physiological action of calcium ions in the presence of magnesium ions. Similar problems are suggested by the wide differences in the degree to which calcium sulphate can neutralize the toxic action of each of the three sodium salts.

That the phenomena exhibited by the roots of plants in their reaction to these various mixed salt solutions are not to be regarded as mere functions of chemical changes in the solution itself is patent. The problem is undoubtedly a much more intricate one, involving chemical reactions of great complexity in the protoplasm of the plant itself. In this connection it is important to call attention to the strikingly similar results obtained by Loeb<sup>3</sup> as to the relative toxic effect upon animals of pure and of mixed solutions.

A pure salt solution, e. g., of sodium chloride, was found to be

<sup>1</sup> Loew (Bul. No. 18, Div. Veg. Phys. and Path., U. S. Department of Agriculture, p. 33), referring to an experiment made by Boehm, appears to doubt the value of calcium in the form of the chloride as a plant nutrient, owing to the formation of hydrochloric acid in the assimilation of calcium by the plant. Here is another suggestion as to the reason for the inferiority of calcium chloride to calcium sulphate in neutralizing the toxic action of salts of other bases.

<sup>2</sup> As has already been noted (under Table VI), a heavy precipitate of calcium carbonate is formed in this mixture, so that it becomes in great part a solution of sodium chloride plus a solid excess of calcium carbonate.

<sup>3</sup> See the papers by this author cited in the Bibliography (p. 58).

strongly poisonous to marine animals in various stages of development—i. e., a fish (*Fundulus heteroclitus*), a jellyfish (*Gonionemus* sp.), and a sea urchin (*Arbacia* sp.). But the addition in small quantity of a salt yielding another kind of cathion, such as magnesium, potassium, and calcium, more or less neutralized this toxic effect, although each of these salts was itself toxic in pure solution. As in the case of plants, calcium was particularly effective. That it is the cathions rather than the anions added to the solution which are chiefly effective as counter agents is evident from the fact that of each base the chloride only was used. Moreover, in only one mixture of three chlorides could fertilized eggs of the sea urchin be brought to an advanced stage of development, but sodium bromide could be successfully substituted for sodium chloride in the mixture.<sup>1</sup> It is clear, therefore, that the anions play a very subordinate part in the physiological action of such mixtures.

Loeb suggests that the physiological effect of a pure solution, whether toxic or stimulating, is attributable to a reaction whereby various cathions which are assumed to enter into combination with the proteids of the organism are replaced by the cathion of the surrounding solution, in accordance with the law of mass. Thus, in case of an animal or organ immersed in a solution of sodium chloride, ions of calcium and of potassium would be forced from their organic compounds and sodium ions would be substituted for them. This would cause a disturbance of equilibrium and finally a cessation of irritability in the tissues. Such effect can be prevented, or, if it has not proceeded to the point of disorganization, counteracted by the addition to the solution of salts containing the corresponding cathions, i. e., potassium and calcium. Hence the author derives his conception of a "physiologically balanced salt solution," examples of which are sea water, the blood of animals, and a mixture of definite concentrations of the chlorides of potassium, sodium, and calcium. The chief function of such a solution is regarded as the maintenance of "a certain physical condition, a certain labile equilibrium, of the protoplasm or the colloids."<sup>2</sup>

From considerations such as these, and from the discovery that a close analogy as to absorption of water exists between the behavior of a frog's gastrocnemius immersed in a solution of a potassium, sodium, or calcium salt and that of potassium, sodium, and calcium soaps,<sup>3</sup> the development of Loeb's theory of the existence and function of "ion-proteid compounds" was logically inevitable. The hypothesis is stated as follows: "Salts or electrolytes in general do not exist in living tissues as such exclusively, but are partly in combination with

<sup>1</sup> Amer. Journ. Physiology, 3, 442 (1900).

<sup>2</sup> Ibid., 3, 445 (1900).

<sup>3</sup> See Pflüger's Archiv, 75, 303 (1899).

proteids. The salt or electrolyte molecules do not enter into this combination as a whole, but through their ions. The great importance of these ion-proteid compounds lies in the fact that by the substitution of one ion for another the physical properties of the proteid compounds change. We thus possess in these ion-proteid compounds essential constituents of living matter which can be modified at desire, and hence enable us to vary and control the life phenomena themselves. \* \* \* If it be true that life phenomena depend upon the presence of a number of various metal proteids (Na, Ca, K, and Mg) in definite proportions, it follows that *solutions which contain only one class of metal ions must act as a poison*. The reason for this is that the one class of metal ions will gradually take the place of the other metal ions in the ion-proteids of the tissues. Even a pure NaCl solution must thus be poisonous, although this salt permeates all our tissues and is the main constituent of the [soluble] inorganic matter of the ocean."<sup>1</sup>

Pauli,<sup>2</sup> who published the same hypothesis almost simultaneously, states his views with greater positiveness. "The general distribution of the ion-proteid compound in the living organism can not be doubted; indeed, we have strong reasons for the assumption that all the proteids of the protoplasm exist there only in combination with ions." And again, "Not salts, but salt-ions, are indispensable to the organism."<sup>3</sup>

Loeb's experiments show that to the same ions or mixtures of ions different animals or different organs or stages of development of the same animal may react in a different manner. This was noted in the case of embryonic as compared with fully developed tissue and with myogenic as compared with nuerogenic contractions. Thus in pure solution magnesium chloride is more favorable to the development of fertilized eggs of the sea urchin than is sodium chloride, although the latter causes while the former prevents rhythmical muscular contraction. On the other hand, as the predominant salt in a triple mixture of chlorides (potassium and calcium being present in much smaller quantity), sodium chloride favors, while magnesium chloride prevents, the development of fertilized sea-urchin eggs.<sup>4</sup> Calcium ions prevent rhythmical muscular contraction, but allow the muscle to retain its irritability much longer than is possible in a solution from

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<sup>1</sup> Amer. Journ. Physiology, 3, 327 (1900).

<sup>2</sup> Ueber physikalisch-chemische Methode und Probleme in der Medizin, 19, Wien (1900).

<sup>3</sup> Loew, although attempting no such extensive generalization, has touched upon the question of ion proteids and their relation to vital phenomena in his discussion of the harmfulness to plants exhibited by magnesium salts in the absence of calcium. (See Bul. No. 18, Div. Veg. Phys. and Path., U. S. Department of Agriculture, p. 42, 1899.) <sup>1</sup>

<sup>4</sup> Amer. Journ. Physiology, 3, 439 (1900).

which they are absent.<sup>1</sup> Results similar to those obtained by Loeb have recently been recorded by other investigators.<sup>2</sup>

That the converse case may also occur is indicated by Loeb's investigations: "Different combinations of ions may exist which all have the same effect. It seems as if the physical condition of the colloids were the essential point and that this might be affected by various ion combinations in the same way."<sup>3</sup>

It is not to be doubted that many peculiarities in relation to ions will likewise be discovered in plants as compared with animals. A case in point is that of magnesium chloride, which in pure solution is eight times as toxic as sodium chloride to roots of the white lupine and of alfalfa while the two salts are about equally toxic when calcium is present. Hence lupine roots react toward these two salts in a wholly different manner than do sea-urchin eggs. Furthermore, a comparison of different plants, one with another, or of different organs or stages of development in the same plant, will surely reveal numerous dissimilarities.

The importance of the ion-proteid theory as an aid to the study of the effects, both toxic and beneficial, which solutions of electrolytes induce in organisms, can hardly be overestimated. It is to be regarded as the only really scientific explanation of this class of phenomena which has yet been attempted. Incomplete as the theory is in its present form, and many as are the anomalies needing further study, we can not but welcome it as a most promising instrument wherewith to attack the vast problem of the physical properties and energies of protoplasm.<sup>4</sup>

Meanwhile it is highly desirable that the study of ion action upon plants be extended. Experiments should be made with a larger number of different ions, and with mixtures containing more than two kinds of cations.<sup>5</sup> It is most essential that many species of plants be tested in order that we may determine what classes of reaction to ions are peculiar to certain groups of organisms and what, if any, may

<sup>1</sup> Festschrift für Adolf Fick, p. 111 (1899).

<sup>2</sup> See the papers of Garrey, Anne Moore, Cushing, Lillie, and Stiles cited in the Bibliography, (p. 56). True has lately experimented with *Cladophora gracilis* grown in various synthetic solutions resembling sea water, and has made the highly interesting discovery that an indefinite prolongation of life could be obtained only when a solution equivalent to sea water in its other components, but containing much more NaCl, was employed. Addition of calcium and potassium salts was found necessary in order to neutralize effectively the toxic action of a sodium salt solution.

<sup>3</sup> Amer. Journ. Physiology, 3, 443 (1900).

<sup>4</sup> For certain limitations of the theory as now formulated reference should be made to the very important paper of Kahlenberg [Journ. Physical Chem., 5, 339 (1901)].

<sup>5</sup> Loeb's discovery that fertilized eggs of the sea urchin could be developed to the pluteus stage in mixtures of three, but not of two chlorides, indicates that much is to be expected from such an extension of these investigations. See Amer. Journ. Physiology, 3, 441, (1900).

be regarded as generic properties of protoplasm. No less important, as Loeb's work with animals has conclusively shown, will be the comparative study of different organs and functions and stages of growth in the same plant, as to their different reactions to the same ions and combinations of ions.

From the point of view of agriculture the ion-proteid theory will doubtless throw light upon much that is now obscure and even paradoxical in the relation between the plant and the soluble components of the soil. Nothing is more certain, in the light of such observations as are recorded in this paper, than the inadequacy of soil physics and soil chemistry alone to explain many details of this relation. The chemistry of protoplasm and its proteid compounds must surely be taken into account before we may hope to get to the bottom of the subject.

#### STIMULATING EFFECT OF DILUTE SOLUTIONS.

As an incident of these investigations it was demonstrated that in the case of certain salts, when plant roots are exposed to pure solutions which are much too dilute to produce any toxic effect, there occurred a decidedly stimulating effect upon growth, as compared with that in the distilled-water control during a corresponding period. As would be expected, this was shown to be the case for salts of calcium, both the chloride and the sulphate acting as stimuli. Here, however, we have to do with salts which contain valuable elements of plant food.

But a marked stimulating action occurs in pure solutions of sodium carbonate (slight in 0.002 normal, marked in 0.00125 normal and of sodium bicarbonate 0.01 normal). The most pronounced effect was obtained in a 0.00125 normal solution of sodium carbonate, the average elongation of the roots in that solution being one and one-half times as great as in distilled water during the same period. In the case of the two carbonates of sodium it seems necessary to regard the effect as one of chemical stimulus, pure and simple. That this is not due to the sodium ions is evident from the fact that very dilute solutions of other sodium salts (sulphate, chloride) gave purely negative results. It was at first thought that the physiological effects of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) were attributable to the presence of hydroxyl ions in the solution, since the corrosive, clearing action of more concentrated solutions of this salt is precisely similar to that produced by potassium hydrate and sodium hydrate. But toxic, as well as stimulating reactions of exactly the same character were obtained with solutions of the bicarbonate ( $\text{NaHCO}_3$ ), in which a large excess of carbon dioxide was dissolved, and which gave no reaction with phenolphthaleine, even at the end of the experiment.<sup>1</sup> In this case the consideration of free hydroxyl

<sup>1</sup>Solutions of sodium carbonate which were many times too dilute to produce a stimulating effect, yet gave a strong reaction with phenolphthaleine.

ions must be excluded. Hence the conclusion seems unavoidable that the carbonic acid ( $\text{HCO}_3$ ) ions produce the stimulating effect, improbable as this would appear. To what agency should be ascribed the characteristic toxic action (so different in kind from that of sodium sulphate and sodium chloride) of stronger solutions of sodium bicarbonate, in which no free hydroxyl could be detected, is a question to which no answer can at present be given.<sup>1</sup>

None of the other salts with which experiments were made in pure solution were shown to stimulate elongation of the roots, although the possibility is not excluded that solutions still more dilute than those employed will give positive results. Magnesium sulphate was found to be indifferent (neither toxic nor stimulating) at 0.0003125 normal, magnesium chloride at 0.000625 normal, sodium sulphate (nearly) at 0.002 normal, and sodium chloride<sup>2</sup> (approximately) at 0.005 normal.

These observations accord with the well-known principle that many violent poisons, if given in sufficiently minute doses, serve as beneficial stimuli. Familiar examples are the action of arsenic, mercury,

<sup>1</sup>In experiments with sodium carbonate and sodium bicarbonate as to their effect upon animals, Loeb encountered a very similar anomaly. The stimulating effect of various hydrates upon the absorption of water by a muscle immersed in a sodium chloride solution was shown to be clearly due to the hydroxyl ions, being equal in amount when equivalent solutions of hydrates were used, irrespective of the character of the basic ions [see Pflüger's Archiv, 69, 10 (1898)]. The similar effect produced by carbonates of sodium and potassium was ascribed to the same factor, the hydroxyl ions (l. c. p. 20). On the other hand, the effect of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) in stimulating skeleton formation in the pluteus of a sea urchin appears to be due to the carbonic acid ( $\text{HCO}_3$ ) ions, since sodium in other forms, as well as hydroxyl in the form of potassium hydrate, gave negative results [Am. Journ. Physiology, 443, (1900)].

<sup>2</sup>Pfeffer [Pflanzenphysiologie, Ed. 2, 1, 425] observes that possibly chlorides (e. g., sodium chloride), like so many other substances, act in dilute solutions as chemical stimuli. Storp [Biedermann's Centralbl., 13, 76 (1884)] obtained a stimulating effect upon the germination of seeds by immersing them in a 0.01 per cent solution of sodium chloride. Jarius [Landw. Versuchsst., 32, 149 (1886)] found that even a 0.4 per cent solution of sodium chloride stimulated the germination of seeds of wheat, rye, rape, maize, beans, and vetches. Jones and Orton (Bul. Vermont Agric. Exp. Station No. 56, p. 12) observed, as a consequence of the application of sodium chloride to land in order to exterminate the weed known as Orange Hawkweed (*Hieracium aurantiacum*), a marked stimulating effect upon the growth of grass in the same field. Peligot [Comptes rendus, 73, 1078 (1871)] suggests that the stimulating effect upon field crops which is sometimes obtained with sodium chloride may be due to its facilitating the decomposition of calcium phosphate and thus increasing the amount of phosphoric acid at the disposal of the plant. Kellner [Landw. Versuchsst., 32, 365 (1886)] attributes to a similar liberation of phosphoric acid the stimulating effects of iron sulphate upon plant growth recorded by Koenig and by Griffiths (see p. 49). Réveil [De l'action des poisons sur les plantes, p. 41 (1865)] found that sodium hypochlorite in a solution of 0.1 per cent stimulates germination and growth, but is injurious, especially to herbaceous plants, when applied in greater concentration.

strychnine, digitaline, etc., upon animals. Numerous investigators have obtained similar effects with plants by supplying them with very small quantities of various substances which can not be regarded as sources of plant food, such as the extremely toxic salts of some of the heavy metals. In practically all such cases, however, it is very probable that considerable hydrolysis had taken place and that the stimulation might well be attributed to the hydroxyl ions thus introduced into the solution.

Raulin experimented extensively with the fungus *Aspergillus* as to the effect of various metallic salts in stimulating or hindering its growth, his being among the first considerable work in this line.<sup>1</sup>

The well-known observations of Frank and Krüger<sup>2</sup> indicate that copper in small quantities (furnished by spraying with Bordeaux mixture) stimulates the growth of the potato, acting favorably upon almost every organ and function, although this metal is well known to be

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<sup>1</sup>Ann. Sci. Nat., sér. 5, 11, 243 (1869).—The sulphates of zinc and of iron were found to produce marked stimulating effect, the former increasing the dry weight of the fungus two to three or even seven times, the latter about twice. In order to show that the acid radicle was not responsible for the results, a corresponding amount (0.06 gram of salt per 1,000 grams of culture solution) of ammonium sulphate was tried, but no stimulation was obtained. To demonstrate still more completely that basic radicles are here chiefly concerned other salts (nitrates of iron and of zinc, zinc acetate, iron citrate) were tried and yielded stimulative effects similar to those of sulphates. In cases where both iron and zinc were added to the same culture solution (e. g., zinc nitrate plus ferric citrate, or ferric sulphate plus zinc acetate, or zinc acetate plus ferric citrate) the stimulating effect was decidedly more marked than when only one base was used. When sulphates of both zinc and iron were present the effect was nearly twice as great as in the absence of the former, and was exactly twice as great as in the absence of the latter. The diminution of the stimulating effect was almost as great if instead of merely withdrawing one or the other base an equal portion of the second base was substituted for the first; in other words, when two parts of zinc (or of iron) were substituted for one part each of zinc and of iron. The stimulating effect of the different salts of zinc expresses itself in a crop from two to four and six-tenths times that of iron in a crop one and four-tenths to two and seven-tenths times as great as in the pure culture solution.

Manganese was found to produce effects similar to those of iron and of zinc, but "less constant, less appreciable." Silica (as silicates of potassium and of sodium) when added to the culture solution increased the dry weight of *Aspergillus* in the ratio of 1.2 or 1.4 to 1.

Raulin wrongly concluded that zinc and silica are indispensable to this fungus, but justly emphasizes "this influence of infinitely small quantities of substances upon vegetation" (l. c., p. 253).

J. Koenig [Landw. Jahrb., 12, 837 (1883)] and Griffiths [Journ. Chem. Soc., 1884, p. 71, and 1885, p. 46] obtained evidence of a stimulating effect of iron sulphate upon the growth of plants by watering soils used in culture experiments with a solution of this salt. On the other hand Kellner [Landw. Versuchsst., 32, 365 (1886)], following the same method of experiment, obtained only negative results.

<sup>2</sup>Ber. d. deutsch. bot. Gesellschaft., 12, 8 (1894).

extraordinarily poisonous to plants.<sup>1</sup> Miani<sup>2</sup> records the interesting observation that in a vapor-saturated chamber the mere presence of copper in the neighborhood of but not in contact with a hanging drop of water containing spores of *Ustilago* and pollen grains of various plants stimulated the germination of the latter. II. Schulz<sup>3</sup> found that alcoholic fermentation is accelerated by the presence of a small quantity of mercuric chloride and of other substances. The development of *Aspergillus* and of *Penicillium* in glycerol cultures was stimulated, according to Pfeffer,<sup>4</sup> by the presence of small quantities of zinc, manganese, cobalt, etc. Subsequently numerous experiments as to chemical stimulation were made by Richards upon fungi.<sup>5</sup>

<sup>1</sup> For a classical discussion of the toxic effect of exceedingly dilute solutions of metallic salts upon the alga *Spirogyra*, see Nägeli, *Neue Denkschr. schweizerischen Gesellsch. f. gesamt. Naturw.*, **33** (1893). Copper in a solution of 1 part to 1,000,000,000 of water was found to be fatal! (l. c., p. 23.) Attention has lately been redirected to the extreme toxicity of copper by Dehérain et Demoussy [*Comptes rendus*, **132**, 523 (1901)] and by H. Devaux (l. c., p. 717). The latter's observation that protoplasm absorbs less copper when exposed during several hours to a large quantity of a running very dilute solution (e. g., of 1 part copper to 400,000,000 parts water) than when placed for a short time in a single drop of a much more concentrated solution (1 part copper to 30,000 parts water) leaves wholly unexplained the negative results as to the extraordinary toxicity of this substance recorded by Miani [*Ber. deutsch. bot. Gesellsch.*, **19**, 461 (1901)], who immersed his subjects for a long period in a single drop of solution. Nägeli's experiments have been more recently repeated (upon *Spirogyra* and other organisms) by Israel und Klingmann [*Virchow's Archiv*, **147**, 293 (1897)], who made careful studies of the "oligodynamic" effects produced by extremely dilute solutions of copper. A noteworthy contribution to this subject by Galeotti has lately appeared [*Biol. Centralbl.*, **21**, 321 (1901)], in which the effect produced by a "colloidal" solution of copper [prepared after the electrical method recently described by Bredig and Müller in *Zeitschr. für physik. Chemie*, **31**, 258 (1899)] is compared with that of an "ionic" solution of copper sulphate containing an equivalent amount of copper. This author found that the former (colloidal) solution plasmolyzed the protoplasm of *Spirogyra* in a dilution (1 gram-atom copper in 12,600,000 to 126,000,000 liters of water) at which the ionic solution (of copper sulphate) produced no effect whatever. He therefore concludes that the action of the colloidal solution is a catalytic one, closely analogous to the catalyzing action of such colloidal solutions (of copper and other metals) upon hydrogen superoxide.

<sup>2</sup> *Ber. deutsch. bot. Gesellsch.*, **19**, 461 (1901).

<sup>3</sup> *Pflüger's Archiv f. die gesammte Physiol.*, **42**, 517 (1888).

<sup>4</sup> *Jahrb. für wiss. Botanik*, **28**, 238 (1895).

<sup>5</sup> *Ibid.*, **30**, 665 (1897). Richards experimented with sulphate of iron and with salts of zinc, cobalt, nickel, and manganese, as well as other substances, using as subjects one species each of *Aspergillus*, *Botrytis*, and *Penicillium*. The estimation of the amount of stimulus obtained was based upon the increase in dry weight of the whole mass of mycelium in the culture as compared with that in a control free from the stimulating substance. Zinc sulphate was found to be the most powerful stimulant, while important results were also obtained with sulphates of iron, cobalt, and nickel. Salts of lithium were likewise very effective. It was found, however, that acceleration of the development of the mycelium was accompanied by an unfavorable influence upon the production of conidia, when salts of zinc or of iron, amygdaline, or morphine were added to the culture solution. In other words, a stimulation of one function or phase of development does not necessarily imply stimulation of the organism as to all its functions.



Recently an important paper upon the effect of certain chemical stimuli upon fungi and algæ has been published by Ōno.<sup>1</sup>

Similar results as to the stimulation of life processes afforded by the presence of small quantities of various non-nutritive substances have been obtained in experiments with animals. Loeb<sup>2</sup> found this to be true of certain acids, hydrates, and mineral salts, the accelerating effect produced by the solutions upon the absorption of water by muscles, the rhythmical contraction of muscles and the segmentation of eggs being attributed to hydrogen ions, hydroxyl ions, or different basic cations, as the case may be.<sup>3</sup>

The as yet obscure problem of the mode of action of chemical stimuli as regards plants has been discussed by Pfeffer,<sup>4</sup> from whom it may be permissible to quote at some length:

"In the regulation of activity chemical stimuli certainly play a very extensive part. It is obviously a matter of chemical stimulation that the seeds of *Orobanche* and of *Lathraea* germinate only upon the roots of host plants, and probably the same occurs with fungi. In the case of initiatory or only regulatory stimuli, there may be partly involved substances which the organism does not necessarily require. In fact, under certain circumstances very different substances can cause an acceleration of activity. \* \* \* These and similar phenomena obviously arise from different causes. Partly it may be a matter of physiological counter reactions, which can also, for example, occasion an increase of respiration, of circulation of the protoplasm, etc., in response to injurious or other action. In other cases a more simple chemical acceleration of reaction may be concerned, as in catalytic action."

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<sup>1</sup>Journ. Coll. Sci. Univ. Tōkyō, 13, 141 (1900). This author experimented with various species of algæ and fungi in order to determine their reaction to minute quantities of the sulphates of zinc, nickel, iron, and cobalt as well as to sodium fluoride, lithium nitrate, and potassium arsenate. He found a marked increase in the total amount of vegetable matter produced in the presence of any one of these substances, the increase in the case of algæ being due, however, to the stimulation of vegetative reproduction rather than to any marked increase in the size of individual plants. The optimum dose for algæ is considerably smaller than that for fungi, 0.0001 gram molecule in most cases proving toxic to the former. Zinc sulphate exerts the greatest stimulating effect. These salts (especially  $\text{ZnSO}_4$  and  $\text{NaFl}$ ) tend to hinder the development of spores in fungi. Copper sulphate and mercuric chloride stimulate the growth of fungi, but not of algæ.

<sup>2</sup>See all the papers of this author cited in the Bibliography.

<sup>3</sup>It is probably worth while at this point to call attention to the fact that in nearly every case where this stimulative effect has been observed, electrolytes have been used which are known to show marked hydrolysis, with the formation either of hydroxyl ions, or more generally, as in the case of salts of the heavy metals, of hydrogen ions. And it may well be that, as in the studies of Loeb, the stimulating effects observed by former investigators may rightly be ascribed in the majority of cases to the presence of these ions.

<sup>4</sup>Jahrb. für wiss. Botanik, 28, 238, 239 (1895).

In another work<sup>1</sup> Pfeffer emphasizes the idea of counter reactions, suggesting that "one has to do in this accelerating stimulation with one of the manifold reactions which serve, through more intensive activity, to counteract as far as possible an injurious influence or to compensate injuries." And again:<sup>2</sup> "Probably this [stimulating] effect results from a general reaction of the organism against injurious substances, since similar effects are induced by ether, alkaloids, etc., effects which also find expression in an increase of fermentation and respiration. \* \* \* It is easy to understand \* \* \* that furthermore such substances as are poisonous only in higher concentration generally occasion no obvious [stimulating] effect."

If it can be shown that such stimulating effect is sufficiently permanent to express itself in a marked increase in the yield of a crop, its economic importance would be obvious. That the presence of a certain amount of calcium salts in the soil may really act as a chemical stimulant to growth, apart from the value of the salts as plant food, or in rendering soluble other nutritive soil components there appears to be some reason to believe. It is not impossible that other substances, even perhaps those salts of magnesium and of sodium which constitute the most noxious components of alkali soils, when present in quantity too small to be harmful, may be actively stimulative rather than merely indifferent to plants. That several of them are likewise valuable as sources of nutritive material is well known. Whether, after all, the distinction between the chemically stimulating effect and the utility as food of certain mineral salts be always as sharp as is commonly supposed, is a question which can not yet be regarded as decisively answered.

#### ECONOMIC IMPORTANCE OF THE RESULTS.

Some of the facts ascertained by these experiments with salt solutions in their effect upon plants have a direct practical bearing upon agricultural conditions and methods in regions where alkali salts are frequent. Attention is particularly directed to the effects obtained by the addition of lime salts to others. Each of the common soluble alkali salts is found to be very injurious when alone, but usually much less harmful when two are mixed, especially when a salt of lime is one component of the mixture. This is strikingly the case with sulphates of magnesium and of sodium, the noxious effects of these salts being enormously lessened by the application of lime, particularly in the form of gypsum or land plaster (the dihydrate of calcium sulphate). Contrary to the general impression, this corrective effect was found in water-culture experiments to be considerably less for "black alkali" (sodium carbonate) than for any of the "white alkali" salts, although even the harmfulness of black alkali can certainly be greatly diminished by the use of gypsum.

<sup>1</sup> *Pflanzenphysiologie* (Zweite Auflage), 1, 374 (1897).

<sup>2</sup> *Ibid.*, p. 409.

The soluble chloride of lime could apparently also be used to advantage upon a soil which is strongly impregnated with alkali. With this salt the best effects would be anticipated when it is used as a remedy for black alkali, although it is likewise a powerful antidote for the chloride and sulphate of soda and of magnesia. But, except in rare instances, the use of chloride of lime upon a large scale is hardly practicable. The little-soluble carbonate of lime is likewise more or less beneficial in all cases except that of black alkali, but it is a much less powerful remedy than is land plaster (calcium sulphate).

Much economic value should attach to an extension of these experiments by using mixtures of more than two salts. It would thus be possible to imitate more closely the conditions which obtain in alkali soils, where several or all of these salts usually occur together. Furthermore, other kinds of plants should be tried in order to determine to what extent plants differ one from another in their power to resist the effect of various combinations of alkali salts. In this connection experiments should be made with wheat, barley, sugar beets, and other important crops of the region, as it may be found that one crop is better adapted than another to withstand the effects of this or that type of alkali soil.

This leads to the possibility of selecting alkali-resistant breeds of each of the leading crops. By observation of a stand of wheat or of alfalfa which has been injured by the "rise of alkali" or by the use of alkaline irrigating water, it is usually possible to find here and there individual plants which have succeeded in surviving the injurious effects of the salts. Similar differences in the power of individuals to resist the action of alkali salts was detected in the culture experiments. By continued selection of the seed of such resistant individuals, sowing it season after season in alkali soil, there is reason to hope that in time a race could be developed and fixed which would flourish in soils containing a greater amount of alkali than can be endured by the ordinary agricultural varieties.<sup>1</sup> It will likewise be very interesting to determine whether a race bred to resist black alkali, for example, will also prove to be proportionately resistant to white alkali, or whether it will be possible and desirable to develop different races to suit different types of alkali soil. An observation already cited (see p. 34) would indicate that the different power of resistance possessed by individuals of the same species of plant is brought out

<sup>1</sup>Observations made by Roos, Rousseaux, and Dugast [*Ann. de la Science Agron.*, sér. 2, 6ième année, 2, 336 (1900)] indicate such differences among the grapes cultivated in Algeria. It was found that of different varieties growing in the same soil the fruit of some absorbed less sodium chloride from the soil than was taken up by others. As the sale of wine containing too high a content of sodium chloride is prohibited by law in France, the economic importance of this discovery is obvious. Although the problem here involved is somewhat different from that of the power of resistance to the poisonous effects of a salt upon the plant, it serves to illustrate the general principle that different individuals or races show marked dissimilarity in their behavior in the presence of a given soil component.

more sharply in the presence of the carbonates of soda than when other "alkali" salts are concerned.

So great appears to be the promise of results to be obtained by breeding alkali-resistant races of the more important field crops of the far western United States, that the Department of Agriculture has already undertaken work on this line. During the past season experiments with this end in view were begun under the direction of Mr. Webber, of the Plant-Breeding Laboratory, Division of Vegetable Physiology and Pathology. It is hoped that they will demonstrate the practical value of this method of approaching the problem.

#### SUMMARY.

As the result of these preliminary studies, the following facts can be regarded as established:

(1) Those readily soluble salts of magnesium and of sodium which are characteristic components of alkali soils are exceedingly injurious to plants when exposed to pure solutions of them of concentration above a minimum which is specific for each.

(2) They are toxic in the following sequence, beginning with the most harmful: Magnesium sulphate, magnesium chloride, sodium carbonate, sodium sulphate, sodium chloride, and sodium bicarbonate.

(3) Calcium chloride in pure solution is ten times less injurious than sodium chloride, and two hundred times less injurious than magnesium sulphate, if chemically equivalent solutions are considered.

(4) Magnesium carbonate in a saturated solution is not markedly injurious, while magnesium bicarbonate in saturated solution acts as a strong poison. Calcium carbonate and calcium sulphate are positively stimulating in saturated solutions, while calcium bicarbonate appears to be decidedly injurious.

(5) The toxic effect of the injurious salts is due very much more to the influence of the cations (derived from the basic radicle) than to the anions (furnished by the acid radicle).

(6) By mixture of equal volumes of two readily soluble salts, or by the addition of a solid excess of a relatively insoluble to a solution of an easily soluble salt, the toxic effect of the more harmful component can in a majority of cases be diminished, or the concentration of the more toxic salt endurable by the roots of plants can be increased.

(7) This increase is much greater in cases where a different kind of cation is added to the solution than when a new anion only is introduced.

(8) Addition of sodium ions to a solution containing magnesium ions in most instances markedly weakens the toxic action of the latter.

(9) Addition of calcium ions to solutions containing either sodium or magnesium ions nearly always counteracts to an extraordinary degree the injurious effect of the sodium or magnesium ions, this beneficial influence being usually much more marked when calcium is furnished as the sulphate than when the chloride is added.

(10) The ameliorating effect of calcium sulphate is much more marked when it is added to sulphates of magnesium and of sodium than when it is mixed with the corresponding chloride. It raises the concentration limit endurable by plant roots in magnesium sulphate four hundred and eighty times, in sodium sulphate more than sixty times.

(11) Even plasmolysis, although supposedly a reaction to purely physical stimuli, can apparently be completely prevented by altering the chemical nature of a solution without materially diminishing its osmotic pressure. At any rate, plasmolysis was not detected in cases where a solid excess of calcium sulphate had been added to a 0.3 or even 0.4 normal solution of magnesium sulphate, although a pure solution of magnesium sulphate is very strongly plasmolyzing at the concentrations named.

(12) Calcium chloride appears to be peculiarly effective in neutralizing the effect of sodium carbonate.

(13) The effect of one kind of ion in counteracting the physiological action of another kind can not be entirely explained by a study of the chemistry of the solution itself, but must in part be referred to complicated changes in the protoplasm of the organisms. The theory that ions furnished by the dissociation of electrolytes form intimate combinations with the proteids of protoplasm, and that their mutually antagonistic effect expresses itself in a replacement of one kind of ion by another as a result of change in the composition of the surrounding solution, would appear to afford the key to this problem.

(14) At a certain degree of dilution all of these salts become indifferent (i. e., neither toxic nor stimulating) in their action upon plant tissues. The maximum concentration of the indifferent solution is likewise specific for each salt.

(15) At a still greater dilution some of them, as the salts of calcium and the two carbonates of sodium, produce a positively stimulating effect upon the growth of roots.

(16) Individual plants show a marked dissimilarity in their power of resistance to the toxic action of the alkali salts. Such individual differences are strikingly accentuated in solutions of sodium carbonate and of sodium bicarbonate of the maximum concentration which will permit any of the roots to retain their vitality.

#### CONCLUSION.

Too great stress can not be laid upon the fact that the experiments upon which the present report is based are merely preliminary. Furthermore, they were designed primarily to afford a standard for comparison of the salts involved. It is not to be expected—indeed, it is assuredly not true—that in the soils containing these salts the conditions are quite comparable to those maintained in the laboratory in the course of these investigations. The physical nature of the soil, as well as the presence of various other soluble substances, renders it

certain that nowhere in the field will these salts be found to have anything like the poisonous effect which they severally exert upon the roots of plants immersed in water solutions. Nevertheless it is only from such experiments, conducted under simplified conditions, that we can draw conclusions as to the actual effect of the components of alkali soils upon plant growth.

It is very desirable that this line of investigation be continued and extended. Further combinations, perhaps of more than two salts, should be tested; an attempt should be made to imitate as closely as possible natural soil conditions; plants in different stages of growth should be tried, for in irrigated regions it often happens that a standing crop is exposed to a varying soil content of soluble salts at different periods of its development. Finally, it is highly important that the experiments be repeated with other plants of widely different relationship and, as far as possible, of actual agricultural importance in the region concerned. For while we may assume for the present that the same sequence of harmfulness of the several salts will obtain in the case of most or all ordinarily cultivated plants, this is open to doubt, and it is quite certain that the actual limits of endurance differ in the case of different plants.

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# FORMATION OF SODIUM CARBONATE, OR BLACK ALKALI, BY PLANTS.

By FRANK K. CAMERON.

## INTRODUCTION.

Considerable attention has been paid within the past few years to the possibility of growing valuable forage crops on some of the alkali soils of the arid West. This subject was first taken up in California.<sup>1</sup> The great value of saltbushes for certain soil conditions and for certain kinds of cattle feeding seems to be well established, but as both Hilgard and Goss<sup>2</sup> have pointed out there is an element of danger, expressed in the prevalent belief that most of these plants, including the greasewood, chico, and other indigenous plants, convert the less harmful neutral salts, such as sodium chloride and sodium sulphate, into alkali carbonates—that is to say, the less harmful “white alkali” is converted into the more noxious “black alkali,” as has been shown by the presence of sodium carbonate immediately under such plants, whereas no trace of it exists some distance away. It may be possible that the plants with their enormous root systems actually gather up minute traces of sodium carbonate, which may be present in lower depths of soil, gradually causing an accumulation at the surface on the decay of their roots and branches. But the generally accepted hypothesis of the conversion of the neutral salts appears more probable, as will be seen in the course of this paper. It would seem probable that plants growing in bunches or mats would be more effective in producing these localized black-alkali spots, but some of the most striking illustrations of this phenomenon have been observed in connection with more upright species, such as *Sarcobatus vermiculatus*, the common “greasewood” of the West.

In the study of the alkali soils of the arid regions the field parties of the Division of Soils have found the local flora of great value in indicating the character of the particular soils where they are found. This apparent relation between the plant and the salts present in the soil became of interest in this connection and was referred to the

<sup>1</sup>University of California, Agricultural Experiment Station, Bul. No. 125 (1899).

<sup>2</sup>New Mexico College of Agriculture and Mechanical Arts, Agricultural Experiment Station, Bul. No. 22, p. 41 (1897).

laboratory for consideration. The results of some preliminary investigations have proved of such interest as to warrant immediate publication.

#### CREOSOTE BUSH.

A specimen of the creosote bush<sup>1</sup> (*Corillea tridentata*) was examined. This, while a desert plant, is said to shun soils where there is much water-soluble salts. Mr. Means states that its presence can be taken as a sure indication of land free from injurious quantities of alkali. It is found in dry, well-drained upland soils.

The material was thoroughly air dried. The leaves and stems were then carefully separated, and both of the separated samples were ground fine in an agate mortar. A portion of each sample was burned to ash. The finely ground air-dried material and the ash were each carefully leached with successive small portions of water until the leachings ceased to show the presence of chlorides. The leachings in each case were then brought together and made up to a volume of 500 cubic centimeters, and the various determinations were made with 100 cubic centimeter portions. The carbonates<sup>2</sup> were determined by titrating with a twentieth normal (N/20) solution of hydrogen potassium sulphate until loss of color, using phenolphthaleine as indicator. So soon as the color had disappeared a drop or two of a solution of potassium chromate was added and the chlorine determined by titrating with a tenth normal (N/10) solution of silver nitrate. The sulphates, when determined, were estimated gravimetrically as barium sulphate in the usual manner. For convenience the acids thus found to be present are stated as the corresponding sodium salts. This procedure seemed to be justified by a subsequent determination of the amount of sodium present in the solution. It is a well established fact, and a familiar one to chemists, that when a salt of an alkali metal is burned down with charcoal or other organic matter a part of the mineral acid is volatilized and driven off, the alkali base forming a carbonate, which is a stable compound even at quite high temperatures. Nevertheless this is a point often overlooked in the discussion of ash analyses. In obtaining the ashes the examinations of which are described in this paper, very great care was exercised to reduce the amount of this loss of the mineral acid as far as possible, and the burning was done at as low a temperature as possible. In some cases the large amount of fused salt in the burning ash coated the charred organic matter in such a way as to render further combustion at a comparatively low temperature quite impossible. In these cases the combustion was stopped, the fused salts leached out with water, and the residue reburned. It seems probable, as will appear from the results which will be presented, that the loss of mineral acids

<sup>1</sup> Collected by Mr. Thos. H. Means near Tempe, Ariz.; kindly identified for us by Mr. F. V. Coville.

<sup>2</sup> Report 64, Division of Soils, U. S. Dept. Agr. (1900); Amer. Chem. Jour., 23, 571 (1900). Bul. 18, p. 77, Division of Soils, U. S. Department of Agriculture (1901).

in the burning of the plant to ash was kept down to a very small percentage by following the procedure described.

The data obtained on examination of the ashes from the creosote bush are presented in the following table:

TABLE XII.—*Analysis of the ash of the creosote bush.*

	Leaves.	Leaves and small stems.	Stems.
Weight of sample, grams .....	8.5659	3.6942	6.6445
Weight of ash, grams .....	.8282	.3795	.3710
Ash, per cent of plant .....	9.66	10.27	5.58
$\text{Na}_2\text{CO}_3$ , per cent of ash .....	8.90	13.18	17.73
$\text{NaCl}$ , per cent of ash .....	5.71	5.37	3.55
$\text{Na}_2\text{CO}_3$ , per cent of air-dried plant .....	.86	1.35	.99
$\text{NaCl}$ , per cent of air-dried plant .....	.55	.55	.19

The dry leaves, which had been ground fine in a mortar, were extracted with distilled water at the room temperature in the manner described above. The extract failed to show the presence of either sodium carbonate or sodium chloride, but appeared to be slightly acid. An extract made by boiling the leaves with water also failed to show any chlorides or carbonates.

From the facts which have been presented it would appear that while the plant does contain chlorine there is no sodium chloride present as such, and therefore it is probable that the chlorine is in organic combination although nothing is definitely known of the presence of such combinations in plants. The sodium is largely in excess of the amount required to balance the chlorine as sodium chloride. This fact was shown by an actual determination of the sodium.<sup>1</sup> It would seem, therefore, that at least a large part of the sodium in the plant is in organic combination, possibly with some organic acid, and, on combustion or ultimate decay of the plant tissues, much sodium carbonate would be formed, as was found to be the case when the plant was reduced to ash in the laboratory.

It is interesting to note that the mineral constituents, as shown by the ash analyses, had accumulated in the leaves to about twice the amount in which they were held by the stems. The difference is very much less, however, if we consider only the water-soluble constituents in the ashes. Assuming, for the sake of argument, that the base in combination with the carbonic acid and chlorine as determined was entirely sodium, its distribution is shown by the following table:

TABLE XIII.—*Distribution of sodium in leaves and stems.*

Part of plant.	Percentages calculated for ash.			Percentages calculated for air-dried plant.		
	From $\text{Na}_2\text{CO}_3$ .	From $\text{NaCl}$ .	Total.	From $\text{Na}_2\text{CO}_3$ .	From $\text{NaCl}$ .	Total.
Leaves .....	3.86	2.25	6.11	0.37	0.22	0.59
Stems .....	7.69	1.40	9.09	.43	.07	.50

<sup>1</sup> Unfortunately it was not anticipated at the time this determination was made that the exact figure would be required in this discussion, and the data were not entered in the laboratory notebook and have been mislaid.

It appears that in the leaves there was about 2.7 times as much sodium as was necessary to balance the chlorine, while in the stems there was more than seven times as much of the base as the acid would require. This suggests the possibility that the chlorine was being eliminated through the leaves, probably in the form of some volatile compound, which may be the source of the odor from the plant. This idea is brought out somewhat more strikingly, perhaps, by noting that the analytical figures given above indicate that the total amount of water-soluble mineral constituents in the leaves is 1.19 times the amount in the stems, but that the amount of chlorine in the leaves is 2.75 times that found in the stems; from which it would appear that the chlorine was being concentrated in the leaves and, as has been pointed out, was there present, in all probability, in organic combination. This is a point which merits further attention, and it is hoped that it will be the subject of a more thorough investigation in the future.

#### GREASEWOOD.

A more thorough examination of a specimen of greasewood<sup>1</sup> (*Sarcobatus vermiculatus*) was made. This is a typical "alkali plant," its presence being usually regarded as a good indication of much water-soluble material in the soil. Mr. Means reports that whenever he has observed it the soil generally shows the presence of sodium carbonate, the only exception being in Montana, where the soluble salts are entirely sulphates. It would appear that this latter statement warrants further examination of the locality mentioned.

The analytical results obtained from examination of the ashes follow:

TABLE XIV.—*Analysis of the ash of the greasewood plant.*

	Leaves <sup>1</sup> and blossoms (1).	Leaves and blossoms (2).	Stems.
Weight of sample, grams .....	10.6395	5.0000	10.6817
Weight of ash, grams .....	2.7505	1.1736	.5274
Ash, per cent of plant .....	25.85	23.47	4.94
Na <sub>2</sub> CO <sub>3</sub> , per cent of ash .....	51.93	57.90	29.46
NaCl, per cent of ash .....	20.47	22.21	14.31
Na <sub>2</sub> SO <sub>4</sub> , per cent of ash .....	7.97	.....	3.69
Na <sub>2</sub> CO <sub>3</sub> , per cent of air-dried plant .....	13.43	13.69	1.45
NaCl, per cent of air-dried plant .....	5.29	5.22	.71
Na <sub>2</sub> SO <sub>4</sub> , per cent of air-dried plant .....	2.06	.....	1.18

<sup>1</sup> Owing to the relatively large amount of fused salts which coated the carbon or other organic matter, this latter could not be completely burned off when reducing such a large sample to ash.

Five grams of leaves and blossoms, by successive leachings with distilled water at room temperature until the leachings aggregated 2 liters, gave (1) 5.81 and (2) 5.68 per cent of sodium chloride. In both experiments the washings showed no trace of soluble carbonates, but were slightly acid. The residue from (1) after ignition gave a trace of sodium chloride and 0.04 per cent of sodium carbonate.

<sup>1</sup> Collected by Mr. Frank D. Gardner near Salt Lake, Utah.

By the method of Carius—that is, heating in sealed tubes with fuming nitric acid and silver nitrate—

(1) 0.2327 gram of leaves and blossoms gave 0.0310 gram AgCl, equivalent to 5.43 per cent of sodium chloride.

(2) 1.0759 grams of leaves and blossoms gave 0.1432 gram AgCl, equivalent to 5.43 per cent of sodium chloride.

From these results it would appear that the plant contains chlorine, but, within the limits of experimental error, all the chlorine is present as sodium chloride, which can be leached out with water at ordinary temperatures. This is probably true of the major part of the sulphates also, although this was not shown quantitatively. A striking feature is the much larger amount of ash from the leaves and blossoms than from the stems and the markedly larger percentage of the alkali salts in the ash of the former. The idea suggests itself that possibly this plant takes up and stores the salts and holds them as such until it is ready to use such part of them as it needs.<sup>1</sup> On the other hand, it may be, for all that we now know, that these salts are present as described only because the plants can not prevent their accumulation, and, so far from being an inherent feature of the plant's economy, it may be a most undesirable accident due to their peculiar environment, but an accident in spite of which these particular plants are able to survive.<sup>2</sup> But, as Schimper<sup>3</sup> has pointed out, this can not be true in all cases, as evidenced by the fact that halophilous plants show a tendency to take up more salts than nonhalophilous species, even when grown in nonsaline soils.

None of the chlorine, apparently, was in organic combination, this

<sup>1</sup>Schimper [Indomalayische Strandflora, p. 12 (1891); Pflanzen-Geographie, p. 99 (1898)] has expressed the opinion that halophytes thrive on salty soils because of a peculiar physiological structure which enables them to reduce to a minimum the evaporation from their leaves and, in consequence, the absorption of the salt solutions in the soil through their roots. The salt content of their sap is thus kept below a certain concentration, although this concentration may, and often does, greatly exceed that which would be determined by "osmotic equilibrium."

Stahl [Bot. Zeitung, p. 139 (1894)] observes that only a few species, such as *Reaumuria hirtella*, described by Volken's [Die Flora der Aegyptisch-Arabischen Wüste, p. 27 (1887)], are known to be able to free themselves from the salt.

Diels [Jahrb. für wiss. Botanik, 32, 316 (1898)] objects that Stahl experimented with cultivated plants and that the retarded root action noted by Schimper does not take place under natural conditions, and that, as a matter of fact, and probably through the agency of malic acid, most, if not all, the halophytes rid themselves of an excess of chloride. Diel's methods of experiment, as well as the conclusions which he draws from his own premises, are criticized by W. Beneke, Jahrb. für wiss. Botanik 36, 179 (1901).

Directly bearing upon this hypothesis is an observation by Detmer [Bot. Zeitung, 42, 791 (1884)] that "organic acids under the condition prevailing for the vegetable organism are in a position to decompose chlorides with a formation of free hydrochloric acid." See also, Osborne, Report Conn. Ag. Ex. St., 1900, p. 441.

<sup>2</sup>Contejean, Geog. Bot., p. 71.

<sup>3</sup>Schimper, Pflanzengeographie, p. 101 (1898).

plant being in striking contrast in this respect to the *Covillea tridentata* examined above.

Another interesting point is that the leachings of the air-dried leaves and blossoms must have contained about three times as much sodium as was necessary to balance the hydrochloric and sulphuric acids present in the plant. The total amount of sodium calculated from the ash analysis would be 8.32 per cent. A direct determination of the sodium made on an aliquot part of the leachings gave 8.55 per cent, while the amount calculated as necessary to balance the hydrochloric and sulphuric acids, as determined by the ash analysis, is 2.68 per cent. The residue after leaching contained practically no chlorine, sulphates, or carbonates. It would appear that in the burning of the plant or in its decay the sodium, which is probably present in organic combination, yields sodium carbonate as a decomposition product, and this in turn is found in the ash or débris. It seems probable that a large part of the chlorine which was originally taken up or at least held by the plant in the form of sodium chloride has been thrown off by the plant in some manner, the sodium being retained in organic combination.

#### ABSORPTION OF MINERAL CONSTITUENTS BY THE PLANT.

Inspection of the analyses of the ashes of plants in general, whether leaves, stems, or in fact any part of the plant tissues, shows that there are more than enough base-forming elements to counterbalance the possible inorganic acids which the results indicate to be present. Moreover, the ashes are alkaline. It is still an open question as to how these bases, which appear in excess, or, more generally, how all the bases, are taken up and assimilated by the plants and what becomes of the acid radicals. While it is possible that some of the alkaline materials may have been absorbed by the plant in the form of carbonates as such, the amount thus absorbed will be relatively very little, for by obvious metathetical reactions or double decompositions there would be formed carbonates of the alkaline metals. These latter would be hydrolized in water to some extent, giving caustic solutions which would undoubtedly corrode the tissues of the plants. The question as to the disposition of the acid residues is then pertinent. Several possible explanations suggest themselves, which seem worthy of attention in this connection.

It is possible that chlorine, for example, which may have been in the acid radical, has been changed by the plant in such a way as to form organic substances, and that these organic substances may be exhaled by the plant as odors or exuded by the leaves or roots. Against the latter suggestion the experiments of Diels<sup>1</sup> indicate that the excretion of such substances by the roots is very improbable. On the other hand, the chlorine or sulphur may be retained in the plant tissues in organic combination in such form that they more or less

<sup>1</sup> Jahrb. für wiss. Botanique, 32, 316 (1898).



completely disappear on combustion, the organic combination volatilizing as such, or by decomposition yielding volatile products containing the chlorine or sulphur.<sup>1</sup> In evidence against this view are the results obtained in the examination of the sample of *Sarcobatus vermiculatus*, where it was found that the total amount of chlorine in the plant, as determined by the Carius method, in which there was afforded no opportunity for any of the chlorine to escape, was the same as the amount leached out of the ashes by water, within the limits of experimental error.

Another idea that presents itself is that the bases and acids are taken up by the plant in the form of salt solutions; that the plant selects and retains the bases and excretes the acid radicals in some manner as acids. It is noteworthy, in this connection, that it has been observed generally in the cases of water cultures that the nutrient solutions gradually become acid unless special conditions are introduced to prevent it. Occasionally, however, cases have been found where the culture solutions actually become alkaline.<sup>2</sup> The point of special importance in this connection is that either a base or an acid radical, more often the latter, is either rejected or ejected by the plant.

It seems to have been generally supposed that the acidity of these solutions was due to organic acids formed and excreted by the plant, but no satisfactory proof for this view has been adduced. The weight of evidence is now decidedly against this view. It is not at all difficult, from the point of view of the chemist, to construct a probable "mechanism" for the phenomena presented, supposing that the plant has selectively retained the basic constituents and excreted the acids, and that the acidity of the culture solutions is due to the free mineral acids. Diels's<sup>3</sup> investigations in this direction are particularly interesting. He found that certain halophilous plants, when placed in distilled water, steadily lost the sodium chloride they contained. He showed that the salt was not excreted as such,<sup>4</sup> and offers as a probable explanation that the greater amounts of malic acid—the formation of which is shown to be a usual accompaniment of growth in succulent plants, such as most of the halophytes are—decomposes the sodium chloride, forming sodium malate and hydrochloric acid, and this latter is possibly excreted by the roots.<sup>5</sup> The solutions become acid, but, on account of the experimental difficulties, it was not definitely proved that the

<sup>1</sup> It is not intended to imply that chlorine and sulphur may not play very different parts in the plant economy, but the general considerations advanced might be true for either of these or other elements.

<sup>2</sup> Witness the classical investigations of Stohmann, Sachs, and Knop, described by Johnson in *How Crops Grow*, p. 180.

<sup>3</sup> Loc. cit. See also Kearney, Contributions from U. S. National Herbarium, Vol. V, No. 5, p. 277 (1900); and Benecke, *Jahrb. für. wiss. Botanik*, 36, 179 (1901).

<sup>4</sup> This point was established as early as 1865 by Wolf, *Landw. Versuchst.*, 7 pp. 20, 211 (1865).

<sup>5</sup> See reference to Benecke on p. 64.

acidity was due to the presence of hydrochloric acid. It is intended that some experiments in this direction shall soon be made in the laboratory.

A somewhat simpler explanation than the one just described may be offered—simpler because it does not require that the plant must first take up the acid radical and then go through the reverse process of exuding it again. It is known with reasonable certainty that a certain amount of hydrolysis takes place in aqueous salt solutions, although the absolute amount may be, and with ordinary strong electrolytes usually is, very small indeed; nevertheless, it does take place to some extent, and it seems not impossible that the plants might show their selective properties in the solution, taking up the base more rapidly than the acid, the latter in consequence being left in greater proportion in the culture or soil solution. Of classical importance in this connection is the work of Kuhn,<sup>1</sup> who found that when maize was grown in a solution containing ammonium chloride, the ammonium residue was partly taken up by the plant and hydrochloric acid remained in the solution. In fact, there does not seem to be any inherent difficulty in supposing that the plant might selectively absorb any ion for which it might have a special predilection. As soon as this ion is removed from the solution the corresponding ion with its opposite charge of electricity must either be removed from the solution by precipitation or volatilization, for example, or it at once reacts with the water. Supposing the ion removed by the plant to be a base, the action of the remaining acid ion on the water must necessarily be accompanied by the liberation of oxygen from the water of the solution. Whether or not any observation of this kind has been made I do not know, but the liberation of the oxygen might very well take place so slowly as to escape detection. The question as to what becomes of the electrical energy on the ion which the plant absorbs will be answered in a consideration of the work energy, heat energy, or other equivalent forms of energy involved in the mechanism of the absorption process, and does not necessarily demand further consideration at this point.<sup>2</sup>

It must be admitted in all frankness that the known facts in our possession are not sufficient to justify a positive opinion as to the views just presented. They seem, however, to be founded on a rational basis and are put forward tentatively as suggestive of possible lines of investigation and the justification for formulating them here will be found in the results of future work. Whatever may be the bearing of this work on the ideas here presented, it can not fail to be of the utmost importance in throwing light upon the difficult problem of plant nutrition.

<sup>1</sup> Henneberg's Journal, pp. 116 and 135 (1864).

<sup>2</sup> These views are not intended to imply that salts can not be taken up as such, even by nonhalophilous plants, under certain conditions. Wolf (loc. cit.) has long since shown that this may be done, and that, moreover, in such cases the process can not be a simple diffusion phenomenon.

From the data presented above it is evident that in the decay of wood or leaves or, in general, of plant tissues, alkaline carbonates are furnished to the soil. It may be that the processes of decay will furnish at the same time organic acids stronger than carbonic acid and in sufficient quantity to combine with all the bases and prevent an alkaline reaction. As has been shown in this laboratory carbonic acid itself may be formed in sufficient amounts to convert all the carbonates to the form of bicarbonates and thus prevent an alkaline reaction. There is not sufficient evidence to justify a positive statement, but it would seem probable that this can not be always the case and that in fact there is alkali formed by the decay of plant tissues. In humid regions the alkali thus formed is removed by leaching or similar processes and by chemical reactions with the other soil components, for which reactions water is necessary.

In the arid regions, such as are found in the western part of the United States, peculiar phenomena, due to the special conditions there existing, have been observed. The indigenous plants which are found on the alkali lands are comparatively few in number, both as to species and as to individuals; others have been artificially introduced. They all have the property of absorbing more or less large amounts of water-soluble mineral salts and on analysis all show characteristically large percentages of bases. When the leaves or débris from these plants have decomposed there is often found greater or less accumulation of carbonates, although before the plant was cultivated that particular region may have been quite free from soluble carbonates. The decay of any organic matter with the accompanying formation of carbonic acid in a soil containing soluble salts of the alkali metals must be expected to result in the formation of soluble carbonates, partly by dissolving lime or magnesium compounds, followed by subsequent metathetical reactions or double decompositions with the alkali salts; more slowly and in lesser degree, perhaps, but nevertheless surely, if the formation of carbon dioxide is continued, by a distribution of the base between the two acids. This last process, however, is probably of decidedly minor importance in the phenomena under consideration.

Owing to the conditions of climate and drainage existing in the arid regions these carbonates when formed are not leached away, as in the humid regions, and gradually accumulate to the more serious detriment of the soil.

#### COMPARISON OF ANALYSES.

For the purpose of comparison, two analyses of greasewood (*Sarcobatus vermiculatus*) ash are here quoted, the first published by Hilgard,<sup>1</sup> and the other by Goss and Griffin.<sup>2</sup>

<sup>1</sup> University of California, Report of Agr. Exp. Sta., p. 142 (1890).

<sup>2</sup> New Mexico College of Agr. and Mech. Arts, Agr. Exp. Sta., Bu. 22, p. 41 (1897).

TABLE XV.—*Two analyses of ash of greasewood plant.*

Constituents.	First analysis.	Second analysis.
Ash of air-dried plants .....	Percent. 12.03	Percent. 13.12
SiO <sub>2</sub> .....	11.81	3.00
K <sub>2</sub> O.....	18.53	22.06
Na <sub>2</sub> O.....	39.45	23.89
CaO.....	1.36	6.52
MgO.....	1.09	1.35
MnO <sub>2</sub> .....		Trace.
Fe <sub>2</sub> O <sub>3</sub> .....	7.06	14.73
Al <sub>2</sub> O <sub>3</sub> .....		
P <sub>2</sub> O <sub>5</sub> .....		
SO <sub>3</sub> .....	3.51	4.12
CO <sub>2</sub> .....	4.93	4.33
Cl.....	0.46	23.80
	15.04	8.01
Oxygen=chlorine.....	103.04	101.81
	3.25	1.81
	99.79	100.00

<sup>1</sup> By difference.

While these analyses differ considerably in details they indicate the same general conclusions; that is, the ash or decomposition products of the plant will yield a very large amount of alkali in the form of carbonates. The figures in Hilgard's analysis, he states, indicate the presence of about 25 per cent of sodium chloride; about 8 per cent of Glauber's salt ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ), and about 39 per cent sodium carbonate. Combining the figures of Goss and Griffin's analysis in the conventional way, we find about 13 per cent sodium chloride and 29 per cent sodium carbonate. The figures are misleading, for they depend upon an arbitrary calculation of the data as salts, and the effect of the other constituents can not properly be ignored. Similarly, but a qualitative comparison can be made from the data obtained by us. If it may be assumed that the leaves and stems are of equal mass in the individual plants when air dried, our results compare quite well with the analyses just cited.

Acknowledgments are due Messrs. F. D. Gardner and Atherton Seidell for assistance in the experimental work described.

## SUMMARY.

It would seem as a result of the experiments described in this paper that in certain cases at least a transformation of neutral salts to the corresponding carbonates through the agency of plant growth is possible and even probable, and that this factor must be taken under consideration in determining the value and use of such plants. Some tentative suggestions are offered as to the disposition of the mineral salts in plant economy, which it is hoped will lead to more exhaustive investigations.

## RESISTANCE TO BLACK ALKALI BY CERTAIN PLANTS.

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By FRANK K. CAMERON.

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### INTRODUCTION.

While working in the San Joaquin Valley, California, during this past summer one of the field parties of the Division of Soils observed three species of plants which appeared to be characteristic growths on soils containing much "black alkali" or sodium carbonate. Superficial examination in the field brought out the fact that the stems and leaves of these three plants were quite acid, in some cases very markedly so. A possible connection was suggested between this fact and the one first noted—that these plants were all found on soils containing much sodium carbonate. Specimens were collected and sent in to the laboratory for further examination. They were kindly identified by Mr. Kearney, of the Division of Vegetable Physiology and Pathology. They consisted of three samples of *Distichlis spicata*, numbered I, II, and III; one sample of *Suaeda intermedia*, which was separated into two portions, the first numbered IV, consisting of the stems alone, and the second numbered V, being composed of leaves alone; one sample of *Atriplex bracteosa*, which was also separated into a portion numbered VI, consisting of stems alone, and a portion numbered VII, consisting of leaves alone.

Samples I, II, and III were thoroughly air dried by being allowed to remain for about two months in the sacks in which they were received at the laboratory. It should be stated that a rough determination of the acidity they displayed was made as soon as they were received in the laboratory, and the results agreed fairly well with those obtained by the more careful examination subsequently made.

Samples IV, V, VI, and VII were found to be very wet and in serious danger of fermenting when received at the laboratory. They were therefore placed in a hot-air oven and dried for several days at from 105° to 110°C. In each case the material was then cut into small pieces and kept in carefully covered beakers, to which, however, the air had free access.

### METHOD OF EXAMINATION.

The method of examination was in all cases to steep the sample, which had been cut into small pieces about a centimeter in length, overnight or for about twenty hours in a convenient amount of dis-

filled water. About 600 cubic centimeters of the supernatant solution was then decanted through a folded filter, and the analytical details carried out with 100 cubic centimeter portions of the filtered liquid. It was thought probable that this procedure would give a close approximation to the soluble salts on the plant or held in its tissues in the form of inorganic salts. The acid material on the surface of the plant was evidently quite soluble in water. It was concluded, as will be shown later, that it was an organic acid, and that in all probability considerable quantities of its sodium or other salts, as well as the acid itself, were on the surface of the plant and dissolved in the water. The amount of free acid was determined by titrating with a solution of potassium hydroxide, which in turn had been carefully standardized by titration against a twentieth normal ( $N/20$ ) solution of acid potassium sulphate. The other determinations were made in the conventional way.

## DISTICHLIS SPICATA.

TABLE XVI.—*Distichlis spicata*.

	Sample I.	Sample II.	Sample III.
Grams of material.....	13.12	35.35	29.48
Cubic centimeters of leachings.....	750	1,250	1,500
Percentage (mineral matter) leached out.....	4.52	5.12	5.73
Cubic centimeters $N/20$ acid equivalent to 1 gram substance.....	23.03	1.16	2.48

	Percent- age dis- tribu- tion.	Per cent in air- dried material.	Percent- age dis- tribu- tion.	Per cent in air- dried material.	Percent- age dis- tribu- tion.	Per cent in air- dried material.
Ca.....	5.62	0.254	2.89	0.148	3.25	0.156
Mg.....	1.86	.084	1.17	.060	2.10	.120
Na.....	41.30	1.867	33.12	1.696	27.24	1.561
K.....	13.40	.606	9.70	.497	12.23	.701
SO <sub>4</sub> .....	4.38	.198	4.69	.240	2.72	.156
Cl.....	33.44	1.511	48.43	2.480	52.46	3.006
	100.00	4.520	100.00	5.120	100.00	5.730
CaSO <sub>4</sub> .....	6.19	.280	6.64	.340	3.83	.219
CaCl <sub>2</sub> .....	10.48	.474	2.58	.132	5.90	.338
MgCl <sub>2</sub> .....	7.25	.328	4.57	.234	8.20	.470
KCl.....	25.52	1.154	18.49	.947	23.27	1.333
NaCl.....	15.22	.688	57.08	2.922	52.03	2.981
Na.....	35.34	1.598	10.64	.545	6.77	.388
	100.00	4.520	100.00	5.120	100.00	5.730

TABLE XVII.—Soil (0-12 inches) in which Sample I of *Distichlis spicata* was found.

	Per cent.		Per cent.
Ca.....	0.48	CaSO <sub>4</sub> .....	1.60
Mg.....	.16	MgSO <sub>4</sub> .....	.75
Na.....	33.77	Na <sub>2</sub> SO <sub>4</sub> .....	5.50
K.....	1.81	KCl.....	3.47
SO <sub>4</sub> .....	5.44	NaCl.....	10.72
Cl.....	8.06	Na <sub>2</sub> CO <sub>3</sub> .....	39.96
CO <sub>2</sub> .....	22.63	NaHCO <sub>3</sub> .....	38.00
HCO <sub>3</sub> .....	27.65		
	100.00	Percentage soluble, 1 gram soil to 20 cubic centimeters water.....	100.00 3.75

The analytical data obtained from an examination of the *Distichlis spicata*—Samples I, II, and III—are given in Table XVI. The most striking point brought out is the very large amount of acid shown to be on Sample I, amounting for 1 gram of the air-dried material to the equivalent of 23 cubic centimeters of a twentieth normal (N/20) acid. This substance was unquestionably an organic acid and a fairly strong one. It did not appear to act on crystals of calcite very readily. This might have been due, however, to the formation of a slightly soluble lime salt, which would protect the calcite from the solvent. The acid very readily decomposed the alkali carbonates and neutralized not only ammonium hydrate but potassium or sodium hydroxide in the presence of cochineal or phenolphthalein as indicator. It will be seen by referring to the analytical figures that a large amount of sodium is left after balancing the acids by the bases found. This would seem to find its readiest explanation in supposing that there was a much greater quantity of the organic acid on the plant than indicated by the equivalent of 23 cubic centimeters of twentieth normal acid, but present in the form of the sodium or other salts. By referring to the analysis (Table XVII) of the soil from which this Sample I of *Distichlis spicata* was taken, it will be seen that there was relatively a very large amount of soluble carbonates present, about 2 per cent of the soil being composed of these substances—an amount which would absolutely prohibit the growth of any ordinary plant, even though much of the salt was in the form of bicarbonate. Much of this material probably came in contact with the grass leaves, in the form of dust or otherwise, with the result that the acid decomposed the carbonates with the formation of salts of the organic acid. These same views seem to hold for Samples II and III as well, but to a lesser extent, as is shown by the quantitative measurements given.

It would appear from what could be learned in the field that this grass, in the locality from which Samples II and III were taken, often carries as much of the acid material as Sample I shows, or even more. Unfortunately for this investigation the most favorable season for securing samples had passed before Samples II and III were gathered and sent in. This subject will receive more careful attention during another field season.

#### ISOLATION AND IDENTIFICATION OF ACID EXUDATION.

Careful attempts were made to isolate or at least to identify this organic acid, but the attempts proved unavailing for several reasons. But very little material was at command when the investigation was taken up. The relatively large amounts of inorganic salts obtained in the water extracts could not be well separated and presented great analytical difficulties in the attempts to isolate so small a quantity of the acid as was at our disposal. Attempts to crystallize the material from solution, either as the acid itself or as a salt, proved disastrous

on account of the rapid and abundant growth of fungi in the solution when evaporation of the solvent at ordinary temperatures was attempted. The solutions of the material failed to give any reactions by which it could be identified as one of the simpler and better-known organic acids. For these reasons efforts to identify it were abandoned temporarily and further work on it postponed until a time when a larger amount of the material could be obtained. It is confidently believed that the experience thus far gained will insure a successful issue to the next attempt in this direction.

#### HYDROSCOPIC SALT ON THE PLANT SURFACE.

The analytical results would indicate that calcium chloride as such was on the grass, but if present no signs of it were observed on the air-dried material. The samples were all thoroughly dry and not the least evidence of any deliquescent substance on the surface was apparent. It should be remembered, however, that the evidence obtained in the examination of the organic acid indicated that the calcium salt was much less soluble than the sodium or potassium salt. In all probability the greater part of the calcium in combination in the solid phase and not in the form of calcium sulphate was present as the calcium salt of the organic acid; and the greater part of the sodium which was assumed above to be in combination with the organic acid was in reality in combination with the chlorine, which the analysis as stated assumes to be combined with calcium.

On the other hand, it has been noticed that this grass when growing in the field is frequently covered with a moist, sticky substance, which there is reason to believe is caused by moisture absorbed from the air by the salts, but only in sufficient quantity to partially dissolve them, making a paste or gummy mixture. So that it is not so improbable that calcium chloride is sometimes formed and is to be found as such on the living plant.

#### SELECTIVE ABSORPTION OF SOIL CONSTITUENTS.

Another point brought out very strikingly by an examination of the analyses is the relatively large amounts of both calcium and potassium found in the leachings from the plants, when the proportion of these elements in the water-soluble portion of the soil is considered. These facts might possibly find an explanation in part in the lesser solubility of the calcium and potassium salts of the organic acid and the accumulation of such salts formed by contact of dust from the soil with the acid. But such reasoning does not afford an explanation of the enormously increased ratio between the chlor ions and the sulph ions found in the plant leachings as compared with the ratio of these substances in the soil. The relative absorptive powers of the plant for these various constituents are probably the controlling factors.



It would seem desirable to give earnest attention to this subject with plants grown under careful supervision in the field or laboratory, as the evidence here presented indicates that the removal or cropping of these plants for any purpose would result in taking from the soil enormous quantities of desirable plant food and the consequent raising of the proportion of undesirable elements in the soil.

#### FUNCTION OF THE ACID EXUDATION.

When the large amounts of soluble carbonates found in the soils upon which these plants grow are considered, and when the disastrous corrosive action of this substance is remembered, the production of the strong organic acid by the plant seems a wise protective measure of nature. The tendency of sodium carbonate to outstrip other salts in accumulating in the very top layers or crusts of a soil and there corroding the root crowns of plants has been frequently noted by all investigators of alkali problems. It would seem that this organic acid is produced by the plant in the manner most favorable to its being brought into contact with the surface sodium carbonate, partly converting this latter to the sodium salt of the acid and partly, in all probability, to sodium bicarbonate, which, there is strong reason for believing, is not itself so harmful to plant growth as the normal carbonate.<sup>1</sup>

#### PHOSPHORUS IN THE PLANT.

In the attempts to identify the organic acid on Sample I, *Distichlis spicata*, some leachings were obtained which contained a small amount of organic matter mechanically suspended, as well as some in solution. They were allowed to stand for several days in an Erlenmeyer flask, the mouth of which was covered with an inverted beaker. A rapid and voluminous growth of fungi was observed. On filtering off a small portion of the solution after it had been standing a day or two a decided though small amount of phosphoric acid was shown to be present. No trace of this substance was found in freshly prepared leachings of the plant. It would seem probable that it was formed as a result of the action of organisms either upon dissolved organic

<sup>1</sup> The especially pernicious effect on plants of carbonate of sodium is in all probability due to the fact that this salt readily hydrolyzes in water with the formation of considerable amounts of sodium hydroxid, and it is this latter substance which is in reality responsible for its great destructive power. Sodium bicarbonate or hydrogen carbonate,  $\text{Na-HCO}_3$ , might be expected to hydrolyze to some extent also, being composed of a strong base in combination with a weak acid: this would be equivalent to a partial inversion to the normal carbonate. But in the presence of so much carbon dioxide as is present in soils this inversion to the normal carbonate would be greatly retarded or altogether prevented. The normal dissociation of the hydrogen carbonate would then be very small indeed and any chemical activity of the compound depending on the formation of ions would be correspondingly small.

matter in the leachings or perhaps upon the organic matter mechanically suspended in the solution. From lack of material it was not possible to determine the amount of phosphorus in the plant, but the qualitative observations cited would indicate that it was present in considerable amount. It should be observed that it was a constituent of the readily water-soluble portion of the soil from which the plant was taken in very small amounts, if, indeed, it were present at all. Attempts to detect it by the phosphomolybdate method failed to show a trace. The remarkable ability of this plant to take from the soil solutions the mineral constituents it needed, in the presence of the enormous excess of other readily soluble substances, is brought out very strikingly in this connection.

For the reasons here presented it would seem that this plant is worthy of the serious consideration of the botanist and physiologist, and is undoubtedly of very great economic importance.

#### ASH ANALYSES.

Ash analyses of all the plants considered in this paper were made, in the hope that some conclusions might be drawn as to the inorganic materials in the plants themselves, and as to how much, relatively, was capable of being removed by leaching. These analyses will not, however, be presented, for it is obvious that they have no value whatever for the purposes here indicated. The mixture of salts on the plants was so large in amount, and fused at so low a temperature, that it quickly coated the organic matter, so that it was necessary to heat to a very high temperature and thoroughly stir the mixture to obtain anything like a thorough combustion of the organic material. This resulted in a very great loss of the salts by volatilization, sodium chloride and potassium chloride being especially important in this connection. Further, the burning of either sulphates or chlorides of the alkalies with organic materials necessarily means the more or less complete volatilization of the sulphur and chlorine, respectively, and the formation of the corresponding alkali carbonates, a point often overlooked in the consideration of ash analyses. As a consequence of these factors, the results obtained would certainly be misleading. It would appear, from the analyses of the ashes of the plants we are considering, that much more of these soluble mineral constituents can be leached from the plants than the plants ever contained, which is an obvious absurdity. For this reason it does not seem worth while to give these ash analyses any further consideration.

## SUAEDA INTERMEDIA AND ATRIPLEX BRACTEOSA.

TABLE XVIII.—*Suaeda intermedia*.

	Sample IV— Stems.	Sample V— Leaves.		
Grams of substance.....	7.61	14.35		
Cubic centimeters of leachings.....	750	750		
Percentage (mineral matter) leached out.....	14.73	23.80		
Cubic centimeters N/20 acid, equivalent to 1 gram substance.....	.84	2.67		
	Per- centage distribu- tion.	Percent- age in air-dried sub- stance.	Per- centage distribu- tion.	Percent- age in air-dried sub- stance.
Ca.....	0.48	0.071	0.15	0.036
Mg.....	.75	.111	.72	.170
Na.....	42.36	6.239	56.18	13.375
K.....	7.20	1.060	4.52	1.075
SO <sub>4</sub> .....	1.43	.211	.87	.206
Cl.....	47.78	7.038	37.56	8.938
	100.00	14.730	100.00	23.800
CaSO <sub>4</sub> .....	1.62	.239	.51	.121
CaCl <sub>2</sub> .....	.00	.000	.00	.000
MgCl <sub>2</sub> .....	2.66	.392	2.35	.559
MgSO <sub>4</sub> .....	.35	.057	.64	.152
KCl.....	13.71	2.015	8.61	2.049
NaCl.....	64.84	9.551	52.33	12.456
Na.....	16.82	2.476	35.56	8.463
	100.00	14.730	100.00	23.800

TABLE XIX.—*Atriplex bracteosa*.

	Sample VI— Stems.	Sample VII— Leaves.		
Grams of substance .....	21.49	17.79		
Cubic centimeters of leachings .....	750	750		
Percentage (mineral matter) leached out .....	4.48	10.24		
Cubic centimeters N/20 acid, equivalent to 1 gram substance .....	1.19	3.61		
	Per- centage distribu- tion.	Percent- age in air-dried sub- stance.	Per- centage distribu- tion.	Percent- age in air-dried sub- stance.
Ca .....	2.32	0.104	0.39	0.040
Mg .....	2.05	.092	3.36	.344
Na .....	37.79	1.693	41.30	4.229
K .....	7.90	.354	5.39	.552
SO <sub>4</sub> .....	4.10	.184	6.60	.676
Cl .....	45.84	2.053	42.96	4.399
	100.00	4.480	100.00	10.240
CaSO <sub>4</sub> .....	5.80	.260	1.33	.136
CaCl <sub>2</sub> .....	1.74	.078	.00	.000
MgCl <sub>2</sub> .....	8.03	.360	7.57	.775
MgSO <sub>4</sub> .....	.00	.000	7.08	.725
KCl .....	15.03	.673	10.27	1.052
NaCl .....	52.18	2.338	53.56	5.485
Na .....	17.22	.771	20.19	2.067
	100.00	4.480	100.00	10.240

In Tables XVIII and XIX are found the data obtained from an examination of the *Suaeda intermedia* and *Atriplex bracteosa*, respec-

tively. For the purposes of this paper they may very well be discussed together. Both analyses show the production by the plants of an organic acid or acids strong enough to decompose alkali carbonates; and that to some extent salts of this acid or acids, as well as the acids themselves, accumulate on the plants. In both plants this acid organic material is accumulated on the leaves rather than the stems, a situation which would seem more favorable for its being brought into contact with the alkali carbonates on the surface of the ground.

The accumulation of considerable amounts of potassium is again a noteworthy feature with these species. In both cases there is an apparently greater proportion of potassium in the water-soluble portions of the stems than in the leaves, when considered in relation to the other elements present; but when considered in relation with the air-dried material as a whole, the amount of potash is about the same in both leaves and stems for each of these plants.

In the case of the stems of *Atriplex bracteosa* the conventional statement of the analytical results as salts would indicate the presence of calcium chloride as such, and on the stems and leaves of both the *Suaeda intermedia* and *Atriplex bracteosa* considerable amounts of magnesium chloride are indicated. That these salts were actually present as such, however, is negatived by the fact that the air-dried samples did not in any case show the presence of any notably deliquescent substance on their respective surfaces after being dried in the oven. The conventional method of statement is again misleading, as in the case of the *Distichlis spicata*, discussed above.

#### SUMMARY.

From the facts which have been presented in this paper the following conclusions seem justified:<sup>1</sup>

1. That the plant species here considered can make a satisfactory growth on soils containing relatively large amounts of soluble carbonates.

2. That this satisfactory growth is probably due, in large measure at least, to the production and exudation by these plants of considerable amounts of soluble organic acids capable of decomposing soluble carbonates, and thus protecting the root crowns from the corrosive action of hydrolized alkalies.

3. That it appears certain that large quantities of the most valuable plant foods are removed from the soil by these plants, and that in any contemplated use of them, involving their cropping or removal from the soil, this factor merits earnest consideration.

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<sup>1</sup>Acknowledgment is due Mr. Atherton Seidell for assistance in making the analyses presented in this paper.

















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